PB-251 203

MOLECULAR SIEVE MERCURY CONTROL PROCESS IN CHLOR-ALKALI PLANTS

M. Y. Anastas

Battelle Columbus Laboratories

Prepared for:

Industrial Environmental Pesearch Laboratory

January 1976

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

096166

PB 251 203

EPA-600/2-78-014
January 1978

Environmental Protection Technology Series

[redacted]

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA REVIEW NOTICE

This report has been reviewed by the U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policy of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/2-76-014

MOLECULAR SIEVE MERCURY CONTROL PROCESS IN CHLOR-ALKALI PLANTS

by

M.Y. Anastas

Battelle Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

Contract No. 68-02-1323, Task 17
ROAP No. 21ADH-008
Program Element No. 1AB014

EPA Task Officer: E.J. Wooldridge

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

January 1976

ABSTRACT

The applicability of the PuraSiv Hg adsorption process to mercury removal from the hydrogen byproduct and the end-box ventilation streams from mercury cell chlor-alkali plants was investigated. The investigation included the analysis of data obtained from testing of a system that is currently in operation and technical information provided by the system vendor together with that available in the open literature.

Although the measurements of mercury concentration in the hydrogen byproduct stream entering the PuraSiv Hg adsorber taken during performance testing of the control unit appear to be in error, measurements of the outlet concentration indicate that a concentration less than 60 ppbv may be achieved.

The economics of the PuraSiv Hg adsorption process were explored. Available data indicate that the operating costs by this process vary between 0.58 and 0.33 per ton of chlorine produced for plants with capacities between 100 and 750 tons per day.

Mercury removal from the hydrogen byproduct stream may also be achieved by either adsorption over treated activated carbon or by scrubbing with depleted brine. Technical and economic data available to the investigator seem to favor the use of these two processes for mercury control although the data base thereon is not sufficiently developed to warrant a meaningful comparison.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
MERCURY-CELL CHLORINE PROCESS MERCURY AIR EMISSIONS AND CONTROL ALTERNATIVES	3
Description of the Mercury-Cell Process	3
Sources of Mercury Emissions	6
Mercury Control Technology in Chlor-Alkali Plants	10
TECHNICAL ANALYSIS OF MERCURY CONTROL BY MOLECULAR SIEVE ADSORPTION	20
General Description of Molecular Sieves	20
Use of Molecular Sieves for Mercury Removal from Gaseous Streams	21
Performance of a PuraSiv Hg Mercury Adsorption System	22
Factors Affecting Performance of Molecular Sieve Mercury Control Systems	31
ECONOMIC ANALYSIS	33
Capital Costs	33
Operating and Maintenance Costs	34
Total Annual Costs of PuraSiv Hg Adsorption	34
CONCLUSIONS AND RECOMMENDATIONS	37
REFERENCES	40
APPENDIX A	
CALCULATION OF AVERAGE MERCURY CONCENTRATIONS AND AVERAGE DAILY EMISSIONS IN MOLECULAR SIEVE ADSORBER OUTLET	A-1
APPENDIX B	
CAPITAL, OPERATING AND MAINTENANCE, AND ANNUAL COSTS OF MERCURY CONTROL PROCESSES	B-1

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/2-76-014	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Molecular Sieve Mercury Control Process in Chlor-Alkali Plants		5. REPORT DATE January 1976 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) M. Y. Anastas		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle-Columbus Laboratories 505 King Avenue Columbus, Ohio 43201		10. PROGRAM ELEMENT NO. 1AB014; 21ADH-008 11. CONTRACT/GRANT NO. 68-02-1323, Task 17
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Task Final; 10/74-11/75 14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		

16. ABSTRACT The report gives results of an investigation of the use of the PuraSiv Hg adsorption process to remove mercury from the hydrogen byproduct stream and the end-box ventilation stream from mercury cell chlor-alkali plants. The investigation included the analysis of data obtained from testing of a system that is currently in operation and technical information provided by the system vendor together with that available in the open literature. Although the measurements of mercury concentration in the hydrogen byproduct stream entering the PuraSiv Hg adsorber, taken during performence testing of the control unit, appear to be in error, measurements of the outlet concentration indicate that a concentration less than 60 ppbv may be achieved. The economics of the PuraSiv Hg adsorption process were explored. Available data indicate that the operating costs by this process vary between $0.58 and $0.33 per ton of chlorine produced for plants with capacities between 100 and 750 tons per day. Mercury may also be removed from the hydrogen byproduct stream either by brine adsorption over treated activated carbon or by scrubbing with depleted brine. Technical and economic data available to the investigator seem to favor the use of these two processes for mercury control, although the data base thereon is not sufficiently developed to warrant a meaningful comparison.

17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Activated Carbon	Air Pollution Control	13B
Mercury (Metal)	Brines	Stationary Sources	07B
Absorbers (Materials)		Molecular Sieves	11G
Chemical Plants		Chlor-Alkali Plants	07A
Chlorine		PuraSiv Hg Unit	
Sodium Hydroxide			

PRICES SUBJECT TO CHANGE

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited	Unclassified	74
	20. SECURITY CLASS (This page) Unclassified	22. PRICE 4.50 - 2.25

LIST OF TABLES

		Page
Table 1.	Estimated Mercury Emissions from a 300 TPD Mercury-Cell Chlorine Plant	9
Table 2.	Approximate Material Balance for Molecular Sieve Adsorption in a 100 TPD Plant	14
Table 3.	Summary of Test Data Obtained from a PuraSiv Hg Mercury Adsorption Process	23
Table 4.	Mercury Emissions from a 200 TPD Mercury-Cell Chlorine Plant	30
Table 5.	Capital Costs of Cooling/Demisting and PuraSiv Hg Adsorption	35
Table 6.	O&M Costs of PuraSiv Adsorption	36
Table A-1.	Calculation of Average Mercury Concentration for Cycle	A-7
Table B-1.	Capital Costs of Cooling/Demisting and List of Equipment	B-3
Table B-2.	Capital Costs and List of Equipment for PuraSiv Hg Adsorption	B-5
Table B-3.	Basis for Computation of Annual O&M Costs	B-7
Table B-4.	Utility Requirements for Cooling/Demisting in a 100 TPD Plant	B-8
Table B-5.	Utility Requirements for PuraSiv Hg Adsorption in a 100 TPD Plant	B-11
Table B-6.	O&M Cost Components for Cooling/Demisting, $1000 (Curve A, Figure B-2)	B-13
Table B-7.	Incremental O&M Costs of Cooling/Demisting Attributed to PuraSiv Hg, $1000	B-14
Table B-8.	O&M Costs of PuraSiv Hg ($1000) Excluding Incremental Cooling/Demisting Costs (Curve C, Figure B-2)	B-15

LIST OF FIGURES

		Page
Figure 1.	Basic Flow Diagram for Chlor-Alakli Mercury-Cell Operation	4
Figure 2.	Mercury Emission Control by Molecular Sieve Adsorption from Hydrogen Byproduct Stream	13
Figure 3.	Mercury Control by Activated Carbon Adsorption	16
Figure 4.	Depleted Brine Scrubbing for Mercury Removal from the Hydrogen Byproduct Stream	19
Figure 5.	Inlet and Outlet Mercury Concentration Profiles for a Molecular Sieve Adsorber - Cycle 1	24
Figure 6.	Inlet and Outlet Mercury Concentration Profiles for a Molecular Sieve Adsorber - Cycle 2	25
Figure 7.	Inlet and Outlet Mercury Concentration Profiles for a Molecular Sieve Adsorber - Cycle 3	26
Figure 8.	Inlet and Outlet Mercury Concentration Profiles for a Molecular Sieve Adsorber - Cycle 4	27
Figure 9.	Inlet and Outlet Mercury Concentration Profiles for a Molecular Sieve Adsorber - Cycle 5	28
Figure A-1.	Effluent Mercury Concentration from PuraSiv Control Unit - Cycle 1	A-2
Figure A-2.	Effluent Mercury Concentration from PuraSiv Control Unit - Cycle 2	A-3
Figure A-3.	Effluent Mercury Concentration from PuraSiv Control Unit - Cycle 3	A-4
Figure A-4.	Effluent Mercury Concentration from PuraSiv Control Unit - Cycle 4	A-5
Figure A-5.	Effluent Mercury Concentration from PuraSiv Control Unit - Cycle 5	A-6
Figure B-1.	Capital Costs of Control of Mercury in the Hydrogen Byproduct Stream	B-4
Figure B-2.	Operating and Maintenance Costs for Mercury Control in Hydrogen Byproduct Stream	B-10

TOPICAL REPORT

on

ENGINEERING ANALYSIS OF THE PURASIV HG ADSORPTION FOR MERCURY CONTROL IN MERCURY-CELL CHLORINE PLANTS

to

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH & DEVELOPMENT
ENVIRONMENTAL PROTECTION AGENCY

from

BATTELLE
Columbus Laboratories

INTRODUCTION

Mercury is a hazardous air pollutant that is emitted from three gaseous streams resulting from the manufacture of chlorine by the mercury-cell process. These are the hydrogen byproduct, end-box ventilation and cell-room ventilation air streams. A number of control technologies are commercially available for the control of the pollutant in the hydrogen byproduct and end-box ventilation streams. Among these control alternatives is adsorption of the mercury vapor in the PuraSiv Hg adsorption process which is designed for recovery of mercury vapor and cyclic regeneration of the adsorbent. Union Carbide Corporation (UCC), designer of the PuraSiv Hg process claims that the level of control of the process is such that the average concentration of mercury in the effluent gas stream is at or below 60 ppbv. The life of the adsorbent is also guaranteed for three years.

In an effort to determine the technical and economic feasibility of the PuraSiv Hg process in its applicability to the stated purpose, the U.S. EPA sponsored the study at hand. It is the objective of this study

to determine (1) the technical feasibility of the control system on the basis of the analysis of data independently obtained from testing of a PuraSiv Hg adsorption system currently in operation and from analysis of information made available by the system vendor and (2) the economics of the system.

MERCURY-CELL CHLORINE PROCESS MERCURY AIR EMISSIONS AND CONTROL ALTERNATIVES

Chlorine may be produced by electrolytic methods from fused chlorides of aqueous solutions of alkali-metal chlorides.[1,2,3,4,5] In the electrolysis of aqueous solutions of potassium or sodium chloride, chlorine is produced at the anode, while hydrogen and potassium hydroxide or sodium hydroxide are produced as a result of processes taking place at the cathode. This requires that the anode and cathode products be kept entirely separate. Consequently, many ingenious cell designs have been developed and refined; all of these have been variations either on the diaphragm cell, or on a cell which employs mercury metal as an intermediate cathode. Historically, these two processes were developed more or less in parallel.[4] In the United States, the mercury process was an early leader, but shrunk to less than 5 percent of the installed chlorine capacity in 1946. The use of the mercury cell since has grown toward 28 percent of the installed U.S. chlorine capacity through 1968. Since then, there has been a negative trend in the use of mercury cells. Chlorine production in 1974 amounted to 33,000 tons per day[6] of which 21 to 23 percent were obtained from mercury cells.[7] During the first three quarters of 1974, demand for chlorine was high and plants were operating at 95 percent of capacity or higher. Since then the operating rate has dropped to 83 percent.[6] While the number of mercury-cell chlorine plants have not increased recently, the introduction of "dimensionally stable" anodes instead of graphite anodes increased the production of chlorine by mercury cell processes.

Description of the Mercury-Cell Process

The use of potassium chloride brines for chlorine production is entirely analogous to that of sodium chloride. The latter will serve as the basis for the following discussion. The basic process flow sheet for the production of chlorine and caustic soda is shown in Figure 1.

Sodium chloride may be obtained from brines or seawater. Whatever the source, solid sodium chloride is the starting material fed to the process.

Purified saturated brine is fed continuously from the main brine treatment section through the inlet end box to the electrolyzer

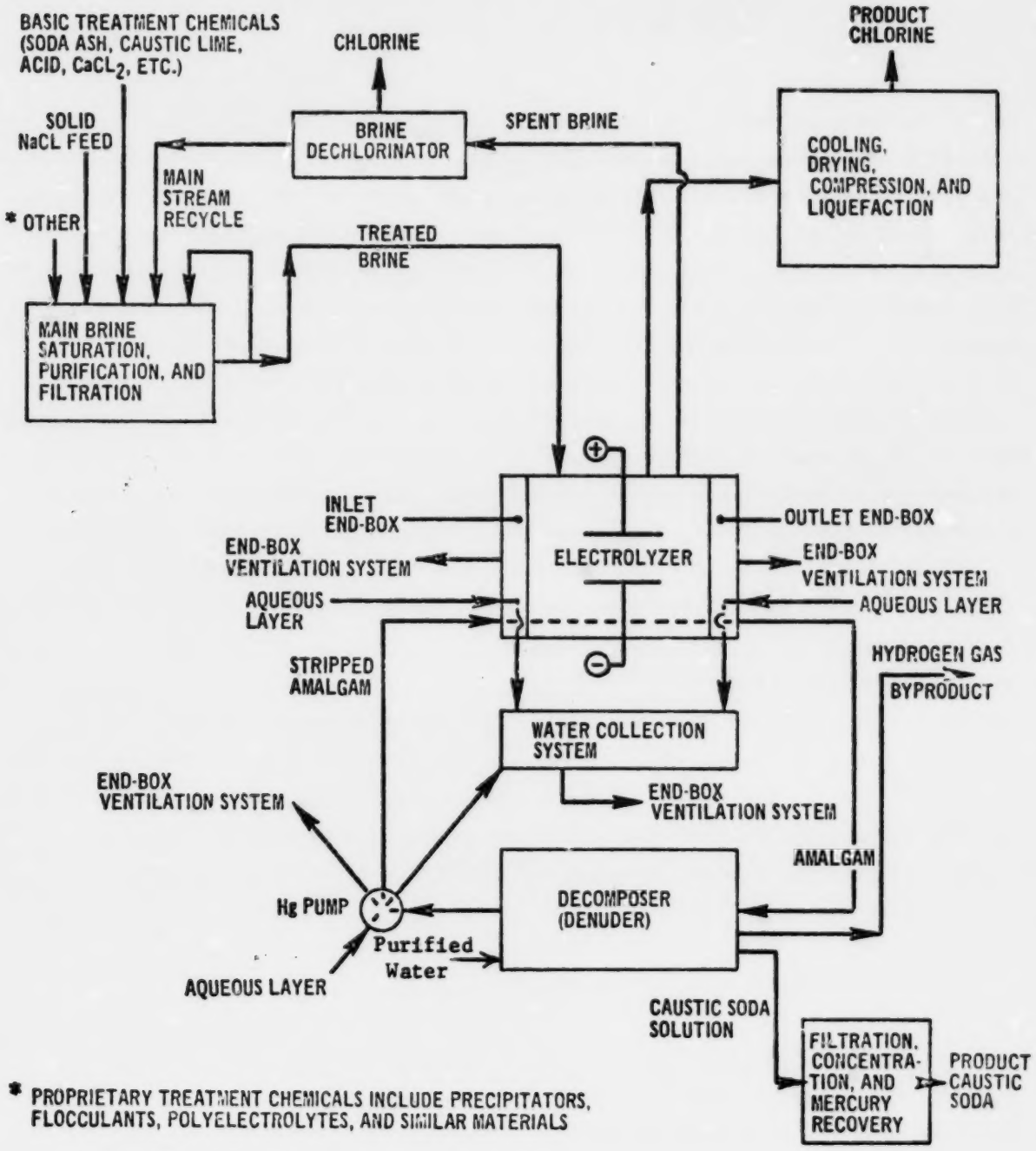


FIGURE 1. BASIC FLOW DIAGRAM FOR CHLOR-ALKALI MERCURY-CELL OPERATION[8]

where it flows between a stationary graphite (or metal dimensionally stable) anode and a flowing mercury cathode. The following reactions take place in the mercury cell:

Anodic half-reaction: $2Cl^-(aq) \rightarrow Cl_{2(aq)} + 2e^-$

$Cl_{2(aq)} \rightarrow Cl_{2(g)}$

Cathodic half-reaction: $2Na^+ + Hg + 2e^- \rightarrow 2Na(Hg)$

Overall cell reaction: $2NaCl_{(aq)} + Hg \rightarrow Cl_{2(g)} + 2NaHg.$

The inlet box is a receptacle placed on the inlet and of the electrolyzer to provide convenient connections for the feed brine and the stripped mercury returning from the decomposer. It also serves to keep the incoming mercury covered with brine. The spent brine is recycled from the electrolyzer to the main brine treatment section of the plant; it may also be sent through a dechlorination step in which it is vacuum treated and/or air blown.

The chlorine gas product formed at the anode leaves the electrolyzer for further treatment. After cooling, the wet gas is dried by scrubbing with concentrated sulfuric acid. The spent acid from this step contains most of the mercury brought along by the wet cell gas. After compression, the dry chlorine gas at elevated pressure either may be used directly or may be subjected to a liquefaction step. It is not known whether there are emissions of mercury to the atmosphere during cleanup of the chlorine prior to sale.

The sodium amalgam flows continuously from the electrolyzer through the outlet end box to the decomposer (denuder) where it is made the anode to a short-circuited graphite or metal cathode (packed bed of chips) in an electrolyte of sodium hydroxide solution. The outlet box is a receptacle placed on the outlet end of the electrolyzer to provide a convenient means to keep the sodium amalgam covered with spent brine and at the same time to permit the physical separation of the two streams. Purified water is fed continuously to the decomposer, where it reacts with the sodium amalgam to produce sodium hydroxide solution as well as byproduct hydrogen gas according to the following reactions. The following reactions

take place in the denuder:

Anodic (mercury) half-reaction: $2Na(Hg) \rightarrow 2Na^{+} + Hg + 2e^{-}$

Cathodic (graphite) half-reaction: $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_{2(g)}$

Overall decomposition reaction:

$$2Na(Hg) + 2H_2O \rightarrow 2NaOH + H_{2(g)} + Hg.$$

The high-purity caustic soda generally leaves the decomposer at the concentration of about 50 weight percent sodium hydroxide.

The caustic soda solution from the decomposer usually is sent to a filtration unit. The solid waste from the filter, which contains the precoat material, is usually sent to an externally fired retort similar to that used for the secondary processing of waste mercury. The mercury thus recovered is returned to the cell for reuse.

Filtered caustic solution at a concentration of 50 weight percent may be concentrated further by evaporation to a 73 weight percent sodium hydroxide product. In some instances, this material is heated to drive off the remaining water in order to produce anhydrous pellets or flakes of solid sodium hydroxide.

The byproduct hydrogen gas from the decomposer may be vented to the atmosphere, burned as fuel, or used as a feed material to a process after removal of the mercury therein.

Sources of Mercury Emissions

The main sources of mercury emissions to the atmosphere from mercury-cell chlorine plants are

(1) The hydrogen byproduct stream

(2) The cell end-box ventilation air stream

(3) The cell-room ventilation air.

The hydrogen byproduct stream leaving the decomposer at 180 F and 1 atm is saturated with mercury vapor and will carry unknown

amounts of mercury in the form of fine droplets which may be an order of magnitude higher than the saturation value. Most of this mercury may be removed by cooling in a surface exchanger to 110 F and passing through a wire-mesh pad mist eliminator. The stream thus treated is saturated with mercury vapor at 10 ppmv and may contain 3 to 10 times the saturation value in the form of mercury droplets most of which are 3 micron in diameter or less. At the 10 ppmv level, the mercury losses will be higher than 5 pounds per day for a 100 ton per day (TPD) plant.

Mercury and mercury compounds leave the cell/decomposer system in the end-box ventilation air. The volume of ventilation air depends upon the age of the plant, the type and specific physical configuration of the cells and end boxes, and the standard operating procedures employed at a particular location.[5] In some cases, the volume flow rate of end-box ventilation air may approach or exceed that of the hydrogen produced in the decomposer. For some new cell modifications currently in operation, the volume of the end-box ventilation air is usually equal to or less than that of the hydrogen byproduct stream. In a certain plant the former is about 80 percent of the latter. Because of the wide variations in end-box construction, it is difficult to specify the emissions. The best current intelligence indicates that the mercury losses sustained in the untreated end-box ventilation air range from about 0.1 to 1.2 pounds per 100 tons of chlorine produced.[4] These values are reasonable in view of the ranges of temperature, degree of saturation, and ventilation-air volume to be expected.

The volume of cell-room ventilation air employed varies from approximately 100,000 to 1,000,000 cfm for a 100 TPD plant.[4,5] A part of this air serves to cool the cells and to keep the cell-room temperature within acceptable limits. The minimum amount of air required for this purpose varies seasonally with geographic location, cell design, and the age of the plant.[5] Additional ventilation air is usually required to remove mercury vapor or compounds from the working environment. Estimates of the mercury losses, under normal conditions of operation, in the cell room ventilation air range from about 0.5 to 5 pounds per 100 tons of chlorine produced for plants of 100 to 150 TPD chlorine capacity. The mercury emissions from plants larger than 100 to 150 TPD chlorine capacity apparently are less than would be indicated by a direct proportion based on increased production capacity. These estimates are consistent with the

approximations obtained by multiplying the ventilation-air volume by the TLV concentration of 50 mg/m^3. On this basis emissions of 0.45 pounds/day for 100,000 cfm and 4.5 pounds/day for 1,000,000 cfm of cell room ventilation airflow may be expected. Thus, for some plants, the losses of mercury in the cell room ventilation air may amount to more than the combined losses in the hydrogen and the end-box ventilation.

Mercury enters the cell-room atmosphere as a result of a number of operations or conditions:

- End box sampling procedures
- Removal of mercury butter from the end boxes
- Cell maintenance and rebuilding operations
- Other maintenance work which exposes the internal surfaces of pipes and equipment
- Accidental spills of mercury
- Cell and mercury pump leaks
- Cell failure, and other unusual circumstances.

The number and variety of sources of mercury in the cell room air indicate that careful plant operation and good housekeeping are essential in order to minimize the amount of mercury emitted into the cell room air. On the other hand, it is extremely difficult to completely eliminate the contamination of the cell room atmosphere with mercury.

Typical emissions of mercury from a 300 TPD mercury-cell chlorine plant are given in Table 1.

TABLE 1. ESTIMATED MERCURY EMISSIONS FROM A 300 TPD MERCURY-CELL CHLORINE PLANT

Steam	Mercury Emission grams per day	Percent of Total
Hydrogen-Byproduct[a]	8,300	89.63
Cell Room Ventilation[b]	900	9.72
End Box Ventilation[c]	60	0.65
Total	9,260	100.00

(a) Saturated with respect to both water and mercury at 110 F and 1 atm. Does not include mercury mist. Reference (4).

(b) Based on a ventilation rate of 1450 cfm per TPD chlorine and a TLV of 50 micrograms mercury per cubic meter at 70 F and 1 atm. Reference (5).

(c) Based on ventilation rate of 8500 scf (60 F and 1 atm.) air per ton of chlorine and a mercury concentration that is 1/10 of saturation @ 110 F.

Mercury Control Technology in Chlor-Alkali Plants

The national emission standard for mercury from stationary sources, including mercury-cell chlorine plants, limits the daily emission to 2,300 grams per day (GMPD).[9] Recently, EPA proposed amendments to this mercury emission standard which would raise the limit to 3,200 GMPD.[10] The 2,300 GMPD limit is divided among the three sources of mercury air emissions such that 1,300 GMPD may be emitted in the cell-room ventilation air and the remaining 1,000 GMPD may be emitted in the hydrogen byproduct and end-box ventilation streams.[9]

Mercury emission control technology that is currently being employed (including the molecular sieve adsorption process) is apparently capable of achieving the 1,000 GMPD limit for both streams in the largest mercury cell chlorine plants (about 750 TPD). As mentioned earlier, primary cooling and demisting are a necessary precursor to the other control techniques as it is capable of reducing the mercury concentration to about 1 ppmv (as vapor). Other alternatives are reportedly available for reducing the latter concentration to below 50 ppbv. If a daily emission of 500 GMPD is allowed for the hydrogen byproduct stream in a 750 TPD plant then an adequate level of mercury control will allow an effluent mercury concentration of about 250 ppbv. For a 100 TPD chlorine plant, a concentration of about 1.0 ppmv may be allowed. When preceded by cooling and demisting the control techniques (molecular sieve and treated activated carbon adsorption and depleted brine scrubbing) to be discussed below are capable of reducing the time-average mercury concentration to below 50 ppbv.

The end-box ventilation stream is usually of the same volumetric flow rate (or less) as the hydrogen byproduct stream. Furthermore, control schemes available for the latter are usually also available for the former.

There are several control processes that are potentially available for control of mercury emissions from the hydrogen byproduct and end-box ventilation air streams by reducing the vapor concentration from 1 ppmv to 60 ppbv. These processes are usually preceded by secondary cooling and demisting. The processes are:

- PuraSiv Hg adsorption
- Sulfur- or iodine-impregnated activated carbon adsorption
- Depleted brine scrubbing
- Hypochlorite scrubbing.

Common to all three processes under consideration are two processing steps prior to mercury vapor adsorption by molecular sieves or sulfur impregnated activated carbon or scrubbing with depleted chlorinated brine. The first step is cooling the hydrogen stream from about 180 F to 110 F using 80 F cooling water followed by mercury mist elimination in a wire-mesh pad mist eliminator. In application of the device for collection of acid mist in sulfuric acid plants, it has been found capable of removing 99 percent (plus) of particles of 3 microns in diameter or greater ($\geq 3\mu$) and 15 to 30 percent of particules $<3\mu$.[11] The concentration of mercury in the stream at this point (110 F, 1 atm.) will be the saturation value of 10 ppmv and (probably) an additional 20 to 30 ppmv (equivalent) in the form of mercury mist. The second step involves compressing the gas to 6 psig in a rotary blower followed by cooling to between 55 F and 65 F and passing it through a tubular type mist eliminator which has a removal efficiency of 99 percent (plus) for particles $<3\mu$ in sulfuric acid-mist removal applications.[11] Measured values of mercury concentration[13] downstream from such a tubular type mist eliminator strongly indicate that the particulate removal efficiencies reported for sulfuric acid mist are applicable for mercury mist since mercury inlet concentrations that are 5 to 10 percent higher than the vapor saturation value were observed.

In what follows the first three control technologies listed above will be described. A flow diagram and approximate material balance for a 100 TPD plant will be given. The design basis for the cooling/demisting step will be as follows.

For all processes considered the cooling/demisting step involved (1) cooling the hydrogen byproduct stream to 110 F at 14.7 psia in the primary cooler from approximately 180 F, (2) mist elimination in a wire-mesh pad demister, (3) compression in a rotary blower to 20.7 psia, (4) cooling to 60 F in the secondary cooler, and (5) mist elimination in a tubular-type eliminator. The pollution control alternatives were assumed to reduce the mercury concentration of about 1 ppmv, obtained after cooling and mist elimination, to 60 ppbv.

PuraSiv Hg Adsorption

A process for control of mercury in the hydrogen byproduct stream has been developed by Union Carbide Corporation (UCC).[13] The mercury vapor (about 1 ppm) is removed from these streams by adsorption over a proprietary adsorbent especially designed for such use.

A typical flow sheet of such a process is given in Figure 2. The purpose of the two-bed system shown is such that at any time one of the beds is undergoing adsorption while the other is undergoing regeneration. The hydrogen byproduct stream is compressed to a pressure between 4 and 8 psig, cooled to a temperature in the range 50 F to 70 F and passed through a tubular type mist eliminator and steam heated to a temperature between 90 F and 100 F before being introduced to the PuraSiv Hg adsorber. Adsorption of the mercury occurs without a significant rise in temperature.

The concentration of mercury in the effluent is guaranteed by Union Carbide to be lower than 60 ppbv on the average. Part of the adsorber effluent (10 to 20 percent of the hydrogen from the decomposer) from the bed in which adsorption occurs is used to regenerate the other bed. In a dual-bed system designed for adsorption over a period of 24 hours, regeneration of the loaded bed is carried out by heating the generation gas to a temperature between 450 to 500 F in an electrical heater and passing it through the bed for about 12 hours. Thereafter, the heater is shut off and the bed undergoes cooling for about 12 hours. The gas from the bed undergoing regeneration is cooled before mixing with the hydrogen byproduct stream from the decomposer.

The process can be designed for a turndown ratio of 5:1. The flow through the rotary blower is the sum of the hydrogen byproduct and the regeneration gas. Hence for the PuraSiv Hg adsorption process the cooling/demisting equipment is 10 to 20 percent larger in capacity. The life of the molecular sieve absorbent is guaranteed by the vendor to be not less than 3 years with effluent discharge of 60 ppbv. This period was used as the design life for the adsorbent. An approximate material balance appears in Table 2.

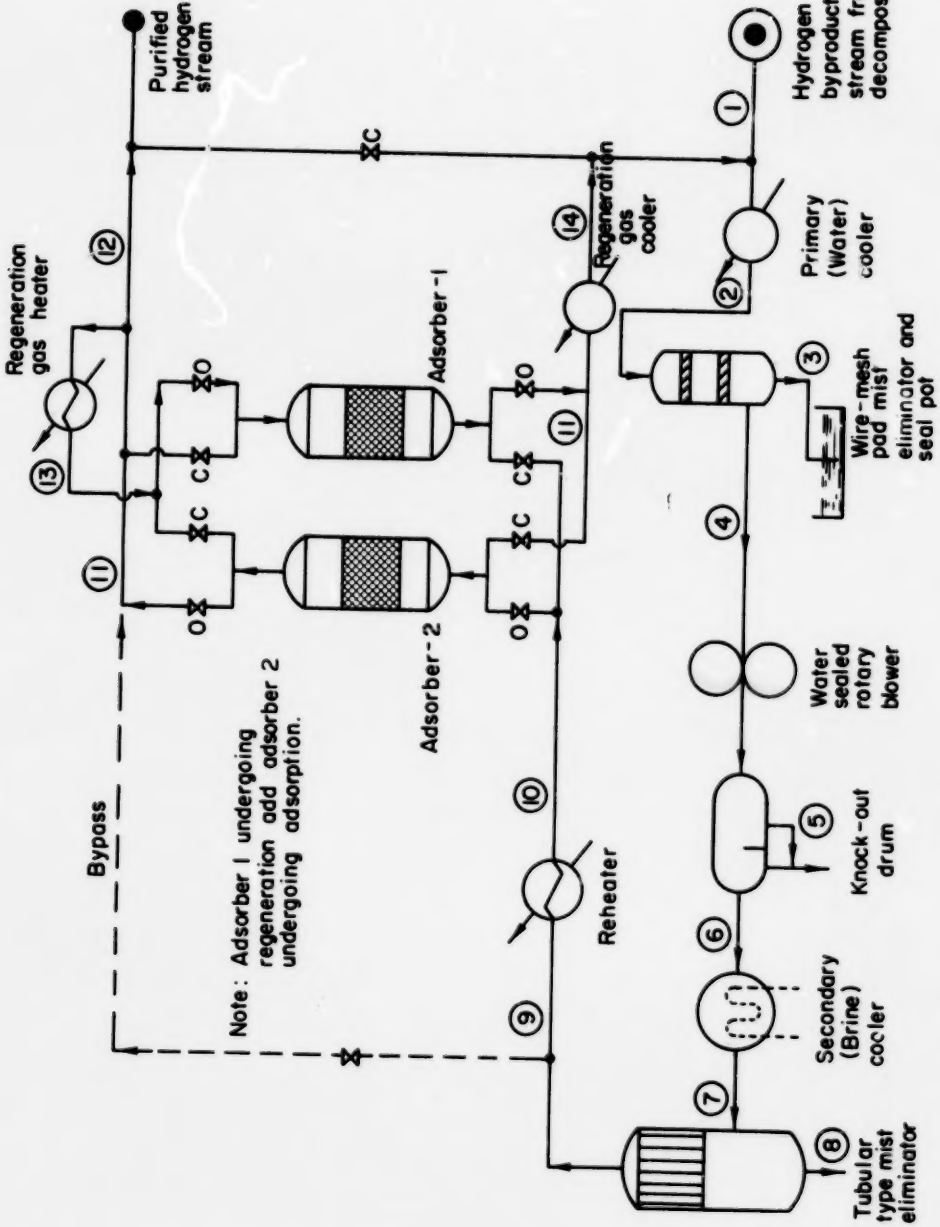


FIGURE 2. MERCURY EMISSION CONTROL BY MOLECULAR SIEVE ADSORPTION FROM HYDROGEN BY-PRODUCT STREAM

TABLE 2. APPROXIMATE MATERIAL BALANCE FOR MOLECULAR SIEVE ADSORPTION IN A 100 TPD PLANT

Stream Number	Stream Description	Press Psia	Temperature F	Mass Flow Rate[a] H_2, lbs/hr	Mass Flow Rate[a] H_2O, lbs/hr	Mass Flow Rate[a] Hg, lbs/day	Volumetric Flow rate, SCFM[b]
1	Hydrogen Byproduct from Decomposer	14.7	180	234.7	2207.0	145.2	1,870
2	Hydrogen Byproduct to the First Mist Eliminator	14.7	110	270.0	231	7.1	935
3	Mercury and Water from Separator	14.7	110	unknown	unknown	unknown	--
4	Gas to Blower	14.7	110	270.0	231	7.1	935
5	Mercury and Water from Knock-out Drum	14.7	110	unknown	unknown	unknown	--
6	Gas to Secondary Cooler	20.7	110	270.0	231	7.1	935
7	Gas to Tubluar Mist Eliminator	20.5	60	270.0	31	0.48	865
8	Liquid Mercury and Water	14.7	60	unknown	unknown	unknown	--
9	Gas to Preheater	20.4	60	270.0	31.0	0.48	865
10	Gas to Adsorber	20.2	100	270.0	31.0	0.48	865
11	Adsorber Effluent	19.6	100	270.0	28.0	0.033	864
12	Purified Gas	19.6	100	234.7	24.4	0.028	751
13	Regeneration Gas	19.6	100	35.3	3.7	0.005	113
14	Regeneration Gas to Primary Cooler	14.7	180	35.3	8.8 (max.)	0.447	113[c]

(a) Obtained at saturated vapor conditions only. Extent of entrainment not known.

(b) At 60 F and 1 atm.

(c) Hydrogen only.

The advantages and disadvantages of utilizing PuraSiv Hg adsorption may be summarized as follows:

Advantages	Disadvantages
1. Guaranteed performance of the adsorption system.	1. Regeneration gas requirements tend to limit the value of the turndown ratio of the system to a maximum value of 5:1.
2. Relative ease of operation and maintenance.	2. Mercury adsorption efficiency is dependent upon the relative humidity of the adsorber inlet gas stream. Control to levels specified by the vendor is necessary.
3. The system does not require special materials of construction. Carbon steel is used throughout.	
4. The recovered mercury is continuously recycled to the manufacturing process.	
5. Applicable for mercury control in end box ventilation air as is in the hydrogen byproduct stream.	

Sulfur-Impregnated Activated Carbon Adsorption

Mercury in the hydrogen byproduct stream can also be removed by reaction with sulfur, to form mercury/sulfur compounds, in sulfur-impregnated activated carbon.[14,15,16] The temperature-enhanced chemisorption at 100 F to 110 F takes place in a one- or two-bed system as shown in Figure 3. In a two-bed system the FRP-lined (fiber glass reinforced plastic) absorbers are in series with provisions for bypass or reversal of the flow through the beds. The FRP lining is necessary to prevent vessel corrosion by the products of reaction that contain sulfur. This scheme is used to effect a maximum (100 percent) utilization and reliability of the adsorption system. However, one-bed systems are currently in use.[15] Here a small fraction of the adsorbent remains unloaded in the "mass transfer zone" and cannot be used since the emissions after breakthrough may exceed allowable limits.

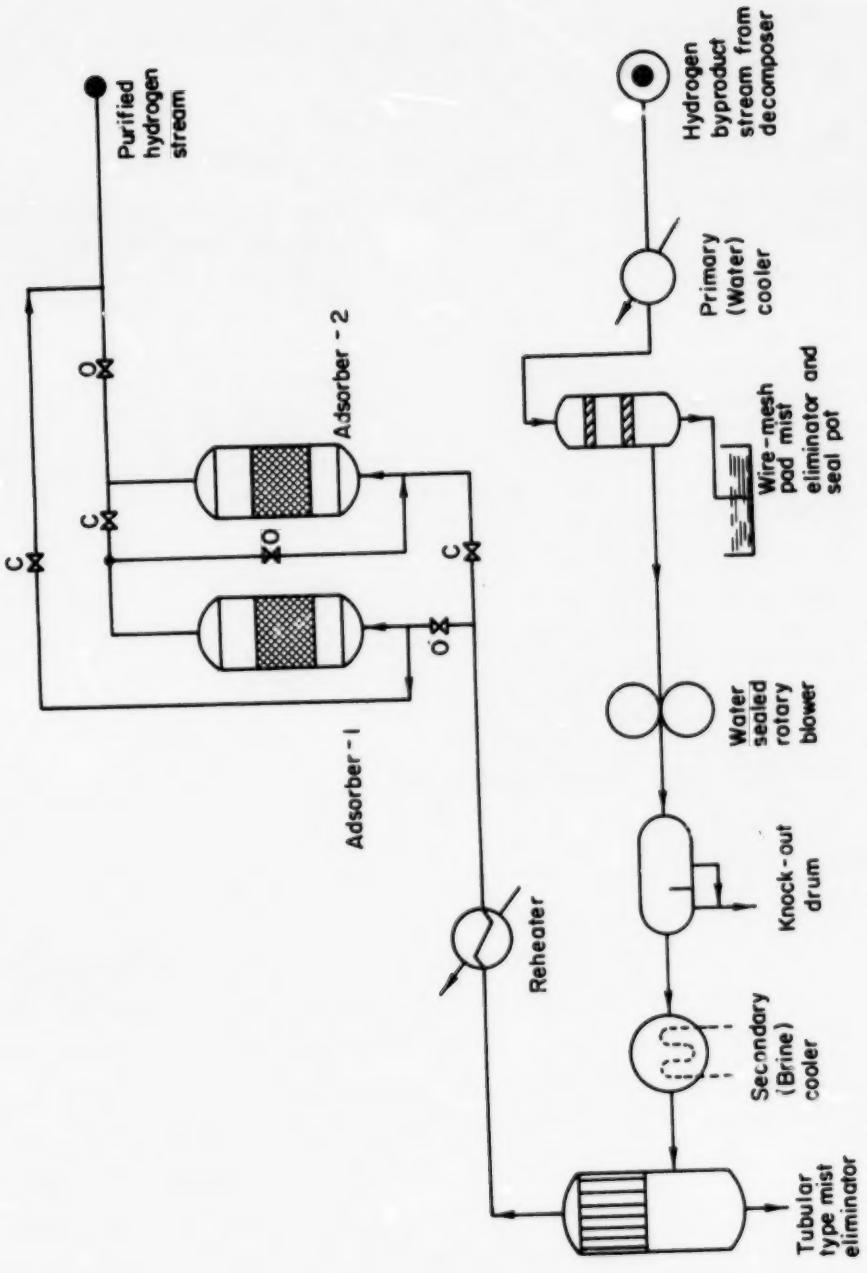


FIGURE 3. MERCURY CONTROL BY ACTIVATED CARBON ADSORPTION

Minor departures from the cooling/demisting steps reported earlier are necessary in this case.[14] Secondary cooling to 50 F and reheating to 110 F are undertaken. The temperature of adsorption should be kept below 150 F since H_2S formation may occur. Calgon, the vendor of the adsorbent, reports typical outlet concentrations below 50 ppbv that may approach 1 ppbv.[15]

A material balance similar to that presented in Table 2 was performed. The only difference here is the absence of recycle. The hydrogen byproduct stream is heated to 100 F before entering the adsorber. A one-bed design was considered rather than two beds in series since operational experience indicates that the reliability, length of service, and adsorbent requirements are satisfactory for such a design.[14] Kinetic considerations seem to dictate the use of an amount of adsorbent that is sufficient for a 3-year service. Thereafter, the adsorbent may be shipped to a processor for retorting of the mercury value therein. The loading capacity of the adsorbent is about 20 pounds of mercury per 100 pounds of adsorbent. Current designs in operation seem to favor a constant pressure drop through the bed. This gives a bed depth of about 4 feet. A gas residence time of 8 seconds in the bed is usually employed.

The projected advantages and disadvantages of utilizing the treated-activated-carbon adsorption process may be summarized as follows:

Advantages

1. Relative simplicity of equipment design and layout.
2. Mercury adsorption to acceptably low levels (reportedly 1 ppb) appears feasible.
3. Ease of equipment operation and maintenance.
4. It is possible that mercury could be recovered by retorting the spent adsorbent, although the economics of such a recovery operation are unknown.

Disadvantages

1. A Fiberglas-reinforced-polyester lining of the adsorption vessel is necessary to prevent corrosion thereof when sulfur-impregnated carbon is used.

	Advantages	Disadvantages
5.	Adsorption process applicable to mercury from end-box ventilation air as well as removal from the hydrogen byproduct.	

Depleted-Brine Scrubbing

Another method of mercury removal involves scrubbing the hydrogen byproduct stream first with depleted brine obtained from the mercury cell and then with 10 percent caustic soda to remove chlorine vapors picked up in the depleted brine scrubber (Figure 4).[4,5,8,17] The cooling/demisting treatment steps are the same as before. The gas is not heated prior to scrubbing. The minimum reported mercury concentration in the scrubber effluent is about 10 ppbv.[8] In a current operation where only depleted brine scrubbing is employed and gas cooling to 80 F is undertaken (in the summertime) scrubber effluent mercury concentrations of about 30 ppbv have been reported.[18] The scrubbers are usually packed columns with a titanium or rubber lining.[2]

However, for purposes of this study, the hydrogen stream at 60 F is contacted with depleted chlorinated brine at 100 to 150 F in the brine scrubber which is operated at an L/G ratio of about 10 to 12 gal per 1000 ft^3. This is followed by scrubbing with 10 percent caustic soda to remove elemental chlorine that volatilizes into the gas in the depleted brine scrubber. A reported L/G ratio in the caustic scrubber is of the order of 20 gal. Depleted brine scrubbing is essentially a closed-loop process. The mercury is recovered in the brine treatment process and in the mercury-cell. Caustic scrubbing appears to consume very little caustic soda because of the reportedly low chlorine concentrations in the gaseous effluent from the depleted brine scrubber.[18] In any case, the caustic scrubber liquid effluent is utilized in brine treatment.

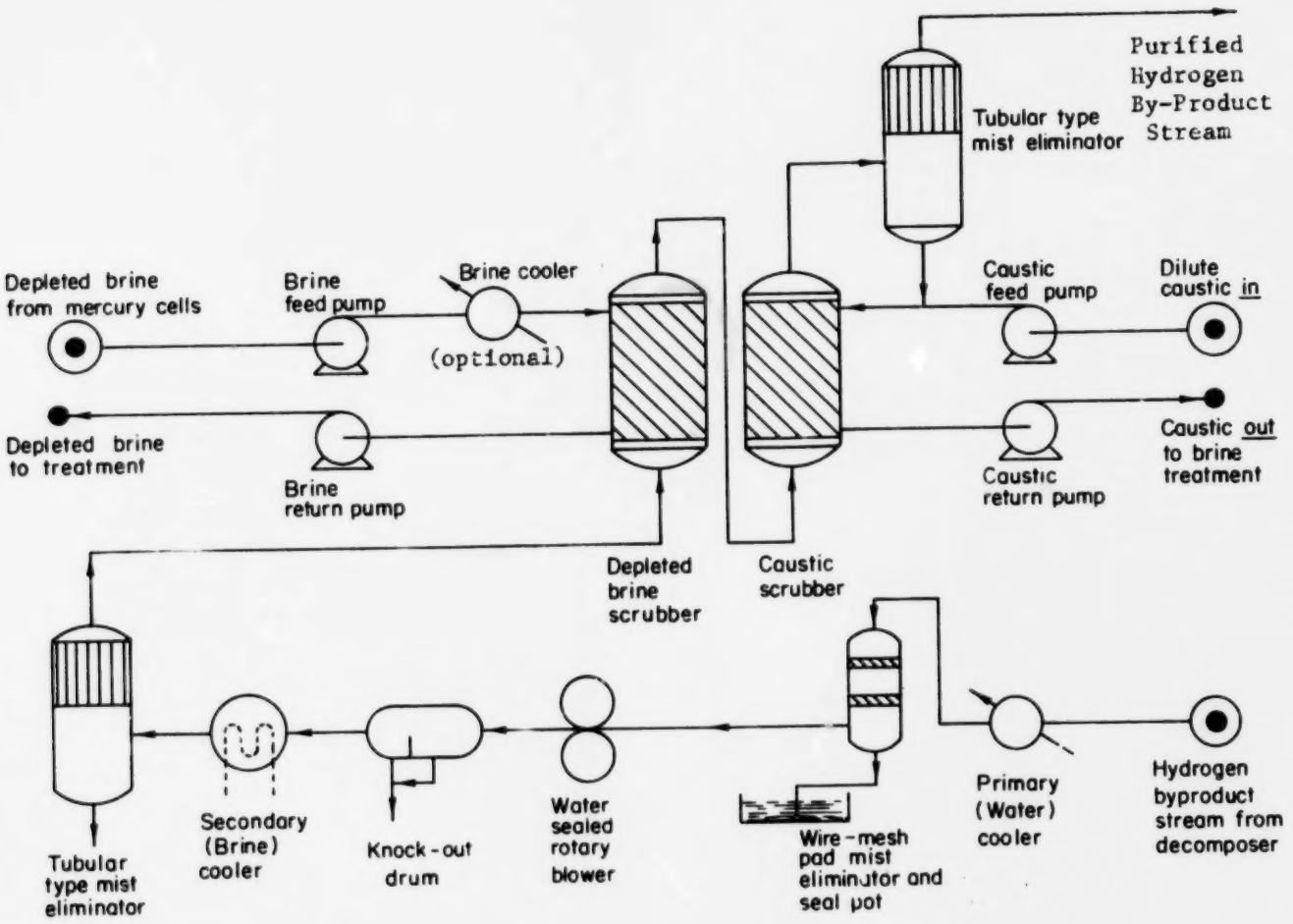


FIGURE 4. DEPLETED BRINE SCRUBBING FOR MERCURY REMOVAL FROM THE HYDROGEN BY-PRODUCT STREAM

The projected advantages utilizing depleted brine scrubbing may be summarized as follows:

Advantages	Disadvantages
1. Process streams used to scrub Mercury and chlorine are obtained from the chlorine/caustic manufacturing process to which they are recycled after use.	1. Mercury removal capabilities are not proved at the present time.
2. Mercury recovery is instantaneous.	2. Corrosion resistant materials of construction are necessary.
	3. Maintenance requirements are relatively high because of (1) above and because of corrosive-fluid pumping requirements.

TECHNICAL ANALYSIS OF MERCURY CONTROL BY MOLECULAR SIEVE ADSORPTION

General Description of Molecular Sieves

Zeolites are crystalline hydrated alumino-silicates of the alkali and alkaline earth elements. Structurally, they are framework alumino-silicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all the oxygens. They may be represented by the general formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

where x is greater or equal to 2 and n is the cation valence.

The framework contains channels and interconnected voids which are occupied by the cation and water molecules.

The term molecular sieve was originated by McBain to define porous solid materials which exhibit the property of acting as sieves on a molecular scale.[16]

There are 100 types of synthetic zeolites. Only a few have practical significance. Uncontrolled dehydration irreversibly alters the framework structure and the positions of the cations such that the structure collapses. To be used as molecular sieves the structure of the zeolite after complete dehydration must remain intact.

Adsorption takes place on external surfaces as well as the internal convoluted surface of the dehydrated microporous zeolite crystal. Because of the inherent characteristics of the crystal structure of the zeolite, the adsorption of a guest molecule depends partially upon its polarity and polarizability.

Use of Molecular Sieves for Mercury Removal from Gaseous Streams

The adsorption of mercury vapor on zeolite molecular sieves has been known for a long time now. Earlier work in this area has been thoroughly reviewed by Breck.[19] He reports that as early as 1909, F. Grandjean found that heated chabazite (a Class I, naturally occurring, molecular sieve with a narrow interstitial channel diameter between 4.89A and 5.58A) had mercury adsorption capabilities. Barrer and Woodhead[20] concluded that the high adsorption of mercury vapor in air on this zeolite was due to a chemical adsorption influenced by the presence of oxygen. The adsorption process was found to be irreversible. However, the adsorption of mercury under conditions approaching vacuum was reversible and the capacity (in grams mercury adsorbed per 100 grams chabazite) of the adsorbent decreased with decreasing temperature. Adsorption data obtained at elevated temperatures showed (after extrapolation) that the mercury adsorption capacity of chabazite at 70 F was in the range 10^{-4} x 10^{-3} gms/100 gms.

Logan[21] studied the adsorption of mercury vapor in hydrogen gas over a synthetic molecular sieve (Union Carbide's 13X) and over chromic acid-impregnated silica gel. At a mercury concentration of about 4.0 mg Hg per m^3 and for breakthrough at a concentration of 0.001 mg Hg/m^3 the

capacity of the molecular sieve was found to be of the order of 10^{-5} to 10^{-4} gm Hg /100 gm. The results for the molecular sieve suggest that water vapor did not seem to affect the adsorptive capacity although the heat of water adsorption caused a 90 F rise in temperature. Furthermore, physical adsorption was seen to occur since the adsorptive capacity increased with a decrease in temperature.

As mentioned earlier, a proprietary synthetic molecular sieve, manufactured by UCC, is commercially available for adsorption of mercury vapor from the hydrogen by-product and end box ventilation streams.[22] The adsorptive capacity of this molecular sieve is orders of magnitude higher than that of 13X.

Performance of a PuraSiv Hg Mercury Adsorption System

The PuraSiv Hg adsorption process is guaranteed by the vendor (UCC) to control the concentration of mercury in the hydrogen byproduct stream to a maximum average of 60 ppbv for a period of 3 years.[22] The control capability claimed for the system was tested by monitoring the mercury concentration in the streams influent to and effluent from the adsorption system installed on a 200 TPD chlorine plant.[12] The results of the test, carried out two years after startup of the adsorption system, are summarized in Table 3. The inlet and outlet concentrations are plotted in Figures 5 through 9.

For purposes of this study, a process that is considered applicable for controlling the mercury content of the hydrogen byproduct stream should be capable of reducing the concentration of the pollutant to below a time average of 60 ppbv. This limit has been arbitrarily set since (1) the vendor of PuraSiv Hg adsorption systems (UCC) claims that such a condition is met by their system and (2) this limit can probably be achieved by alternative control technologies, namely, treated activated carbon adsorption and depleted brine scrubbing.

TABLE 3. SUMMARY OF TEST DATA OBTAINED FROM A PURASIV HG MERCURY ADSORPTION PROCESS[a]

Cycle	Time, hrs during 24-hr cycle	Adsorber Inlet Conditions					Adsorber Outlet Conditions			
		Ave. Pressure, in., Hg[a]	Ave. Temp., F[a]	Measured Ave. Conc., ppbv[a]	Hg Conc. at Saturation, ppbv[b]	Flow Rate, scfm[c]	Ave. Temp., F[a]	Ave. Pressure, in. Hg[a]	Measured Ave. Hg Conc., ppbv[a]	Flow Rate to Boiler Vent, scfm[d]
1	0-2	39.2	72	963	1,397	2,431	95.5	38.1	55.4	1,466
	3.5-5.25	39.1	72	938	1,400	2,412	95.5	38.1	3.1	1,457
	6.5-8.5	39.1	72	876	1,400	2,467	95.5	38.1	<0.1	1,457
	9.67-11.67	39.2	72	900	1,397	2,513	95.5	38.1	0.3	1,452
	12.5-14.5	39.1	72	1,146	1,400	2,461	95.5	38.1	<0.1	1,452
	15.75-17.75	39.1	72	1,219	1,400	2,414	95.5	37.9	1.1	1,452
	18.67-20.67	38.8	71	958	1,346	2,383	96.0	38.1	95.9	1,452
	22-24	38.6	71	965	1,353	2,386	95.5	38.1	429.5	1,454
2	0-2	38.6	71	976	1,353	2,386	95.5	38.1	57.4	1,465
	3-5	38.5	71	954	1,357	2,377	95.5	38.1	58.6	1,466
	5.75-7.75	38.4	71	846	1,360	2,354	95.5	38.1	0.4	1,466
	9-11	38.5	71	841	1,357	2,350	95.5	37.9	0.2	1,466
	12-14	38.5	71	840	1,357	2,350	95.5	36.6	0.2	1,357
	15-17	38.4	71	907	1,360	2,350	95.5	37.9	0.4	1,221
	18-20	38.4	70	992	1,297	2,285	95.5	37.9	26.4	1,221
	21-23	38.4	72	668	1,426	2,330	95.5	37.9	38.6	1,349
3	0-1.75	38.3	71	1,053	1,364	2,395	95.5	38.1[e]	55.0	1,457
	2-3.25	38.6	70	837	1,291	2,334	95.5	39.3[e]	1.9	1,465
	4.25-6.25	38.6	70	828	1,291	2,351	95.5	39.3[e]	0.4	1,466
	7.25-9.25	38.6	71	707	1,353	2,403	95.0	39.6[e]	0.1	1,466
	10.25-12.25	39.3	71	806	1,329	2,356	95.0	38.9	0.1	1,466
	13.25-15.25	39.4	71	761	1,326	2,323	95.0	38.9	0.2	1,414
	16.25-18.25	39.3	70	878	1,268	2,325	95.0	38.9	0.2	1,191
	19.25-21.25	39.3	70	949	1,268	2,370	95.5	38.9	8.1	1,468
4	0-2	39.4	71	945	1,326	2,378	95.5	39.1	4.7	1,459
	3-5	39.4	71	727	1,326	2,382	95.5	39.1	0.2	1,465
	6-8	39.5	70	873	1,261	2,483	95.5	39.1	0.1	1,466
	9-11	39.7	70	923	1,255	2,567	95.5	38.9	0.1	1,467
	12-14	39.5	70	787	1,261	2,515	95.5	38.9	0.1	1,465
	15-17	39.5	70	830	1,261	2,442	95.5	38.9	0.1	1,459
	18-20	39.7	71	937	1,316	2,483	95.5	38.9	3.6	1,457
	21-23	39.7	71	1,067	1,316	2,446	95.5	38.9	120.1	1,457
5	0-2	39.4	71	1,243	1,326	2,408	95.5	39.1	37.4	1,457
	3-5	39.4	71	1,054	1,326	2,406	95.5	39.1	0.2	1,457
	6-8	39.5	71	1,267	1,323	2,397	95.5	39.1	0.2	1,457
	9-11	39.5	71	1,176	1,323	2,368	95.5	39.1	0.1	1,457
	12-14	39.4	71	1,155	1,326	2,373	95.5	39.1	0.1	1,457
	15-17	39.4	71	1,231	1,326	2,324	95.5	38.9	0.1	1,457
	18-20	39.2	71	1,058	1,333	2,322	95.5	38.9	11.0	1,457
	22-24	39.1	71	1,145	1,336	2,296	95.5	38.9	425.9	1,457

(a) Source: Reference 12.

(b) Obtained for mercury vapor pressure in mm Hg between 32 and 300 F. $\log_{10}P = -3212.5/T + 8.025$, where T is °K, Kirk & Othmer Encyclopedia of Chemical Technology, Second Edition, 1967, Volume 13, p 221.

(c) Obtained from Reference 2 but adjusted to standard conditions at 1 atm and 60 F.

(d) Obtained from data on chlorine production reported in Reference 12 and by assuming a factor of 180.16 scfm per ton per hour.

(e) These values are incorrect.

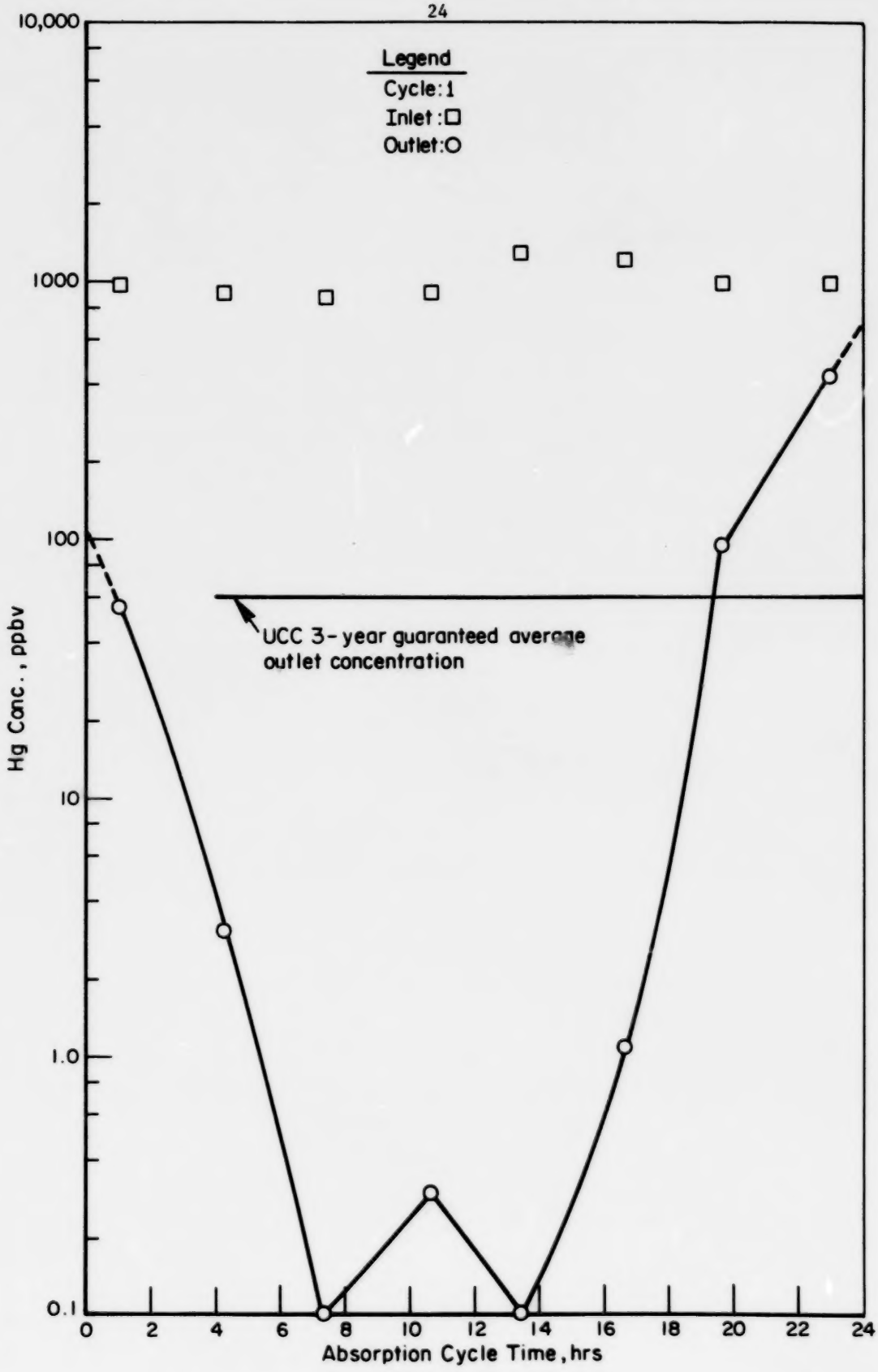


FIGURE 5. INLET AND OUTLET MERCURY CONCENTRATION PROFILES FOR A MOLECULAR SIEVE ADSORBER

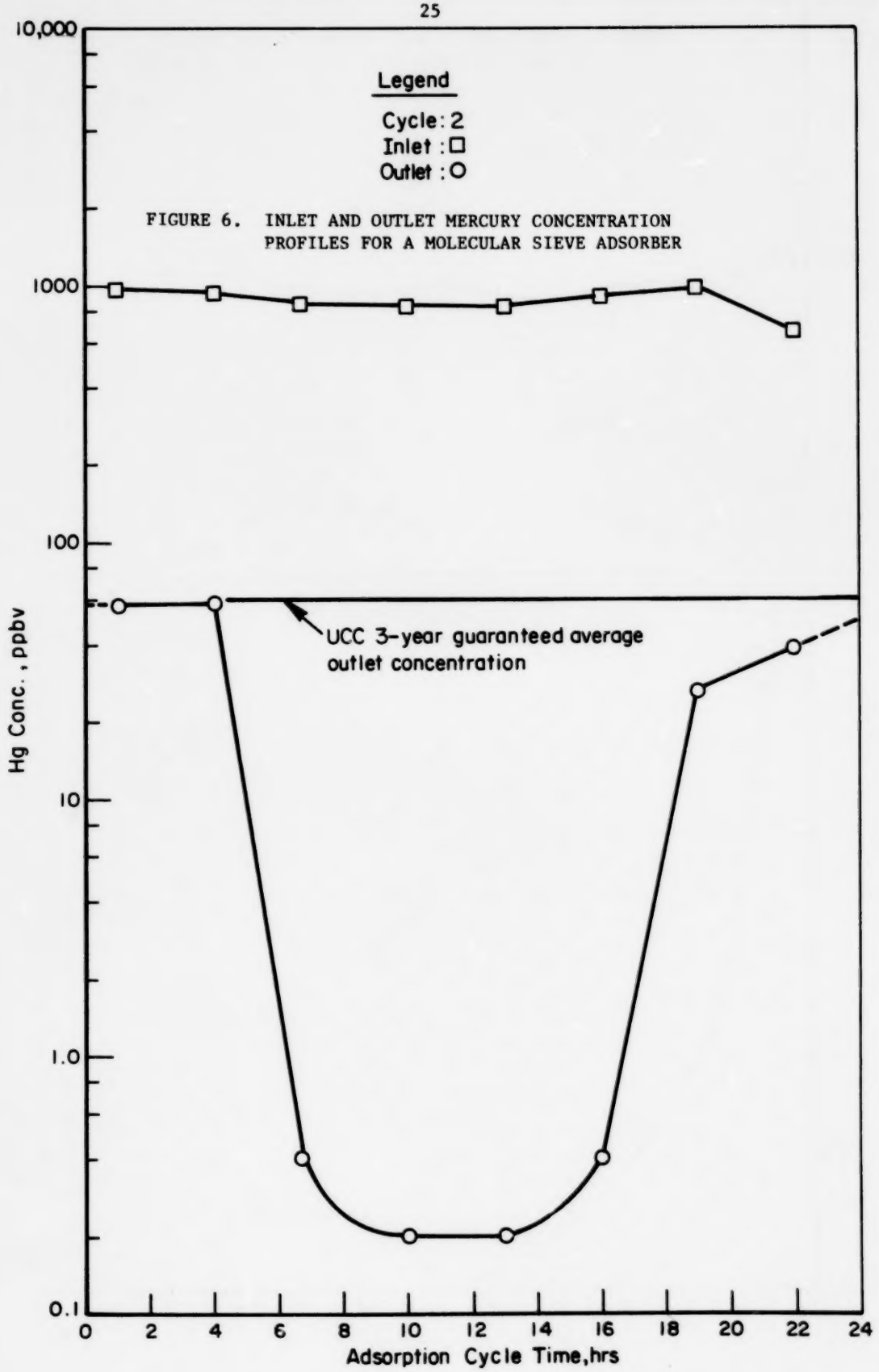


FIGURE 6. INLET AND OUTLET MERCURY CONCENTRATION PROFILES FOR A MOLECULAR SIEVE ADSORBER

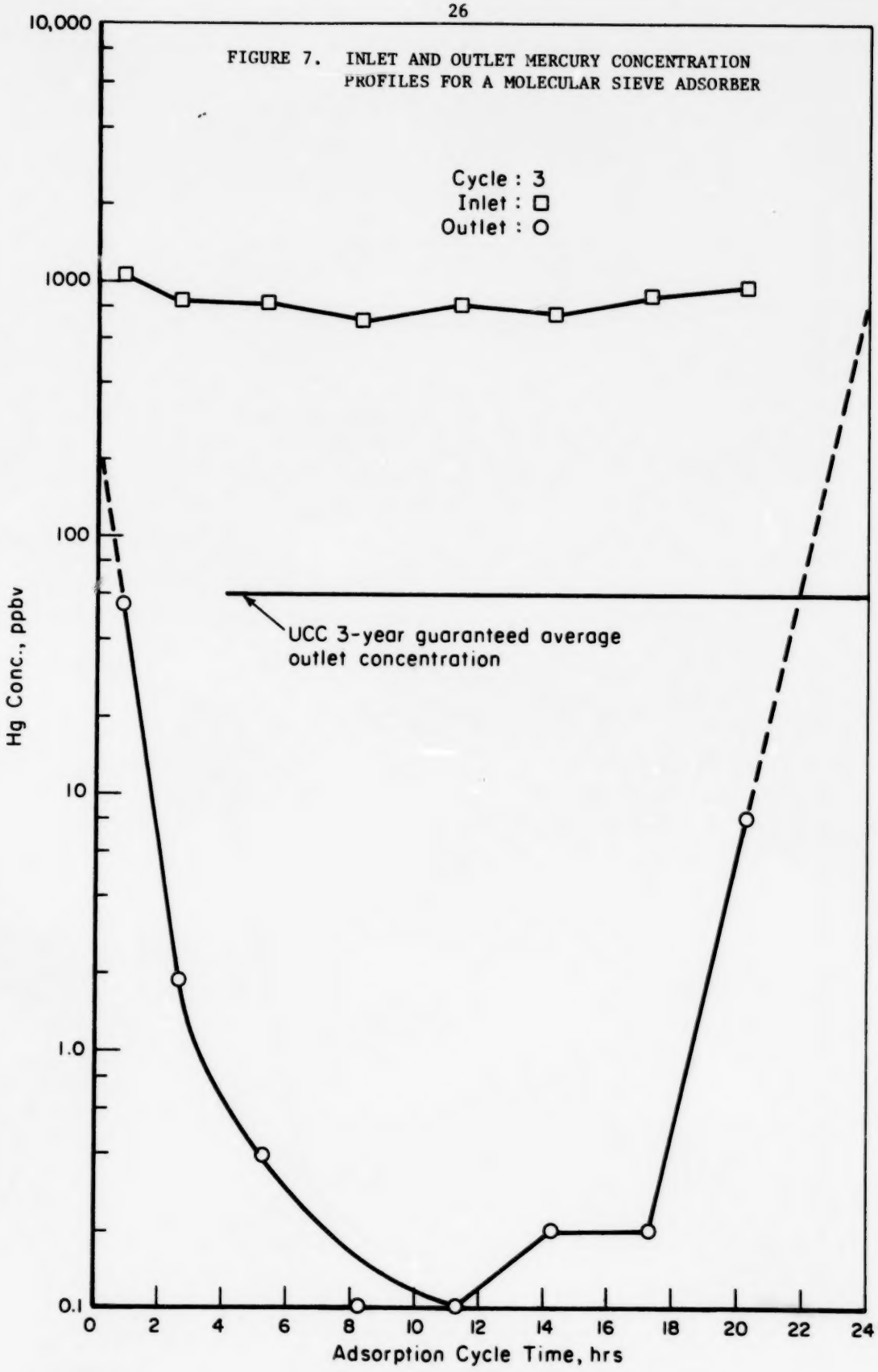


FIGURE 7. INLET AND OUTLET MERCURY CONCENTRATION PROFILES FOR A MOLECULAR SIEVE ADSORBER

FIGURE 8. INLET AND OUTLET MERCURY CONCENTRATION PROFILES FOR A MOLECULAR SIEVE ADSORBER

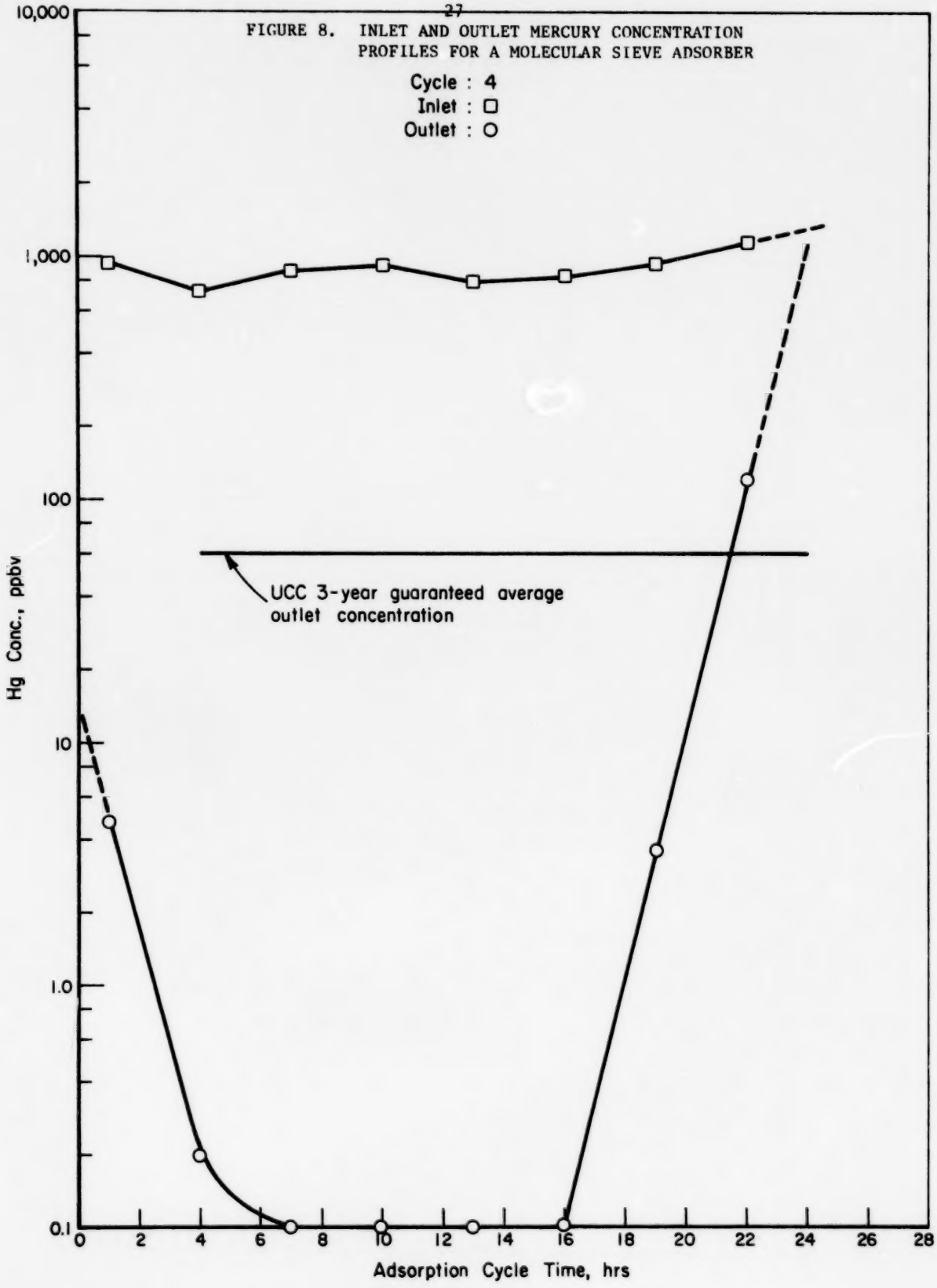
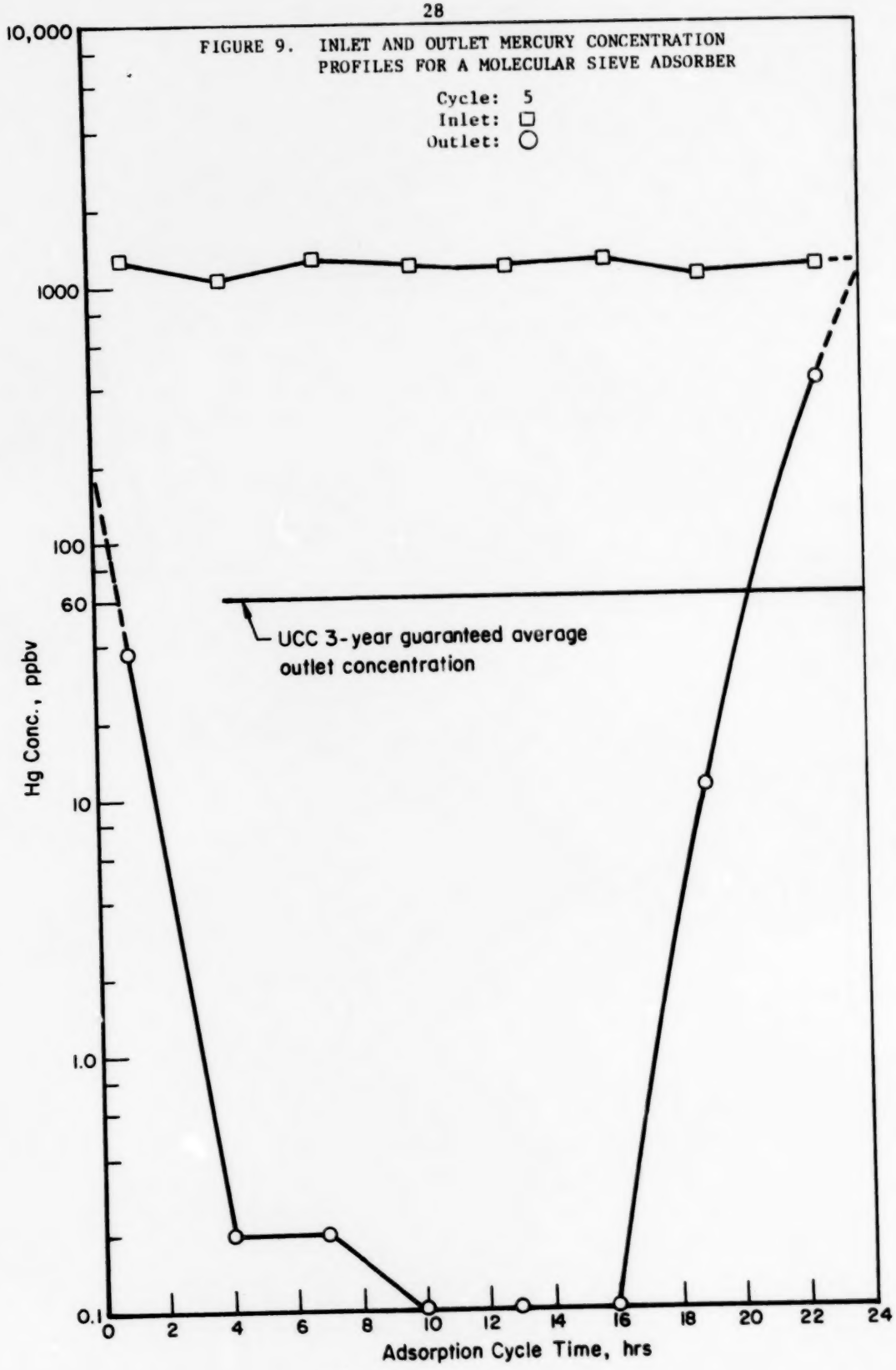


FIGURE 9. INLET AND OUTLET MERCURY CONCENTRATION PROFILES FOR A MOLECULAR SIEVE ADSORBER



UCC's claim was tested through measurements of mercury inlet and outlet concentrations in a PuraSiv Hg adsorption system used to control mercury emissions in a 200 TPD plant. With the exception of the third cycle the measurements of concentration were taken over five characteristic 24-hour cycles of adsorption. The third cycle was terminated after 22.5 hours because of an unscheduled plant shutdown. Mercury outlet cycle - average concentrations were obtained by integration of the profiles given in Figures 5 through 9. The procedure is explained in Appendix A. The amount of mercury emitted was calculated from this average concentration and the average hydrogen flow leaving the system. The results are given in Table 4. Upon inspection of the values of average concentration given in Table 4, it may be seen that except for the first two cycles, UCC's guarantee of the outlet concentration was met after 2 years of service. The average concentration was 65 percent higher than the guaranteed 60 ppbv for the first cycle and 25 percent higher for the second cycle.

The PuraSiv Hg system which was tested on behalf of EPA as a background to this analysis was operated at mercury levels beyond those normally expected in a mercury-cell chlorine plant of the stated capacity--namely 200 TPD. This situation arose as a result of complications caused by an anticipated expansion of the chlorine-producing capacity of the plant.[27] As a result, abnormally large quantities of hydrogen were being recycled. At the time the testing was in progress the hydrogen flow to the adsorber was about 2400 SCFM. UCC-recommended design criteria[13] predicted a flow of about 1700 SCFM. Furthermore, secondary cooling to about 72 F was employed instead of the recommended cooling to 60 F. These two factors tended to increase the amount of mercury flowing into the adsorber. Since the hydrogen stream always is saturated with mercury, the increased flow through the cooling/demisting equipment causes an increase in the total amount of mercury to the adsorber. It is estimated that about 150 percent more mercury was carried to the adsorber as a result of this mode of operation.

The PuraSiv Hg system that was the subject of EPA testing reportedly has been overdesigned with respect to the amount of adsorbent used therein. Although this has been confirmed by the system designer-UCC, no information on the system "overdesign" has been made available.

TABLE 4. MERCURY EMISSIONS FROM A 200 TPD MERCURY-CELL CHLORINE PLANT

Number of 24-Hour Test Period	24-Hour Average Chlorine Production, rate TPD	24-Hour Mercury Emission, gm	24-Hour Average Mercury Concentration, ppbv
1	194	49.6	99
2	183	35.4	75
3	190	16.3	33
4	198	19.1	37
5	194	26.0	51

The results of testing indicate that the guaranteed average mercury concentration of 60 ppbv was being achieved by the adsorption system after 2 years of operation. However, it was not possible to verify UCC's claim that such effluent mercury levels could be achieved after 3 years of system operation.

The mercury inlet concentrations obtained from Reference 12 are too low as a result of experimental error. This is immediately apparent upon comparison of the data on inlet concentration with the saturation value at the reported inlet stream temperature and pressure. The measured value should be higher than the saturation value.

Factors Affecting Performance of Molecular Sieve Mercury Control Systems

The performance of the molecular sieve adsorbent used in control of mercury in the hydrogen stream is affected mainly by (1) the number of adsorption/regeneration cycles to which it has been subjected and (2) the concentrations of mercury and water vapors in the influent stream.

The adsorption system design is such that a maximum average effluent mercury concentration of 60 ppbv is guaranteed for a period of 3 years.[22] With the passage of time this average concentration of the effluent is expected to gradually increase from a level which is well below that guaranteed to one which is close to it. This loss in performance is directly caused by the gradual, but cumulative, destruction of the micropores of the adsorbent as a result of its exposure to the relatively high temperature swings between the regeneration temperature of about 500 F and the adsorption temperature of about 100 F. Investigators of the Bureau of Mines[23] studied the sulfur dioxide adsorption/desorption characteristics of UCC synthetic molecular sieve 13X. The adsorption experiments were carried out at a temperature of 79 F and a total pressure of 26.38 in. Hg for sulfur dioxide concentrations ranging from 1 to 9 percent by volume. The space velocity employed was of the order of 400 vol/vol/hr. The time for complete saturation or loading of adsorbent with sulfur dioxide

was about 36 minutes. The observed loading ranged from 27 to 30 lb SO_2 per 100 lb adsorbent, being higher for the feed richer in SO_2. Desorption (or regeneration) for about 2.3 hours was carried out at tmperatures of about 700 F while the space velocity of nitrogen purge gas was maintained at 4 vol/vol/hr. A 60 percent drop in the capacity of 13X was observed after 13 cycles of adsorption/regeneration. Thereafter the capacity of the molecular sieve seemed to stabilize at the lower level. While no independently obtained information on the long-term effects of cyclic heating (regeneration) is available for the molecular sieve under consideration, field tests carried out by UCC indicate a 10 percent loss in loading capacity over a period of 2 years. Two types of loss in activity may occur for the adsorbent. The first may be a short-term loss taking place during earlier cycles as observed for 13X. The second may be a long-term loss as reported by UCC. Both of these, however, can be anticipated by system design. Analysis of data on effluent mercury concentration from a molecular sieve adsorption unit indicates that the design does anticipate this loss in activity as evidenced by cycle average concentrations that are usually lower than that guaranteed [60 ppbv] by UCC. Field tests indicate that a 2-year sieve life is demonstrated.

Unspecified concentrations of water vapor in the gas stream undergoing adsorption affect the performance of the molecular sieve by reducing its selectivity toward mercury. The condition of relative humidity of the hydrogen stream to the adsorber is considered proprietary by UCC. High water concentrations increase the amount of adsorbent needed to remove a given amount of mercury. While no data on the effect of relative humidity on adsorption capacity are available, it has been found that a design relative humidity of 50 percent does not adversely affect the selectivity to the point where "uneconomical" loadings are produced.

ECONOMIC ANALYSIS

In this section an evaluation of the economic feasibility of mercury control by PuraSiv Hg adsorption is developed and discussed. While a comparison of the capitalized costs of this system with other potentially available alternatives (treated activated carbon adsorption and depleted brine scrubbing) would be useful in assessing their economic feasibility, the lack of an adequate data base on the cost and performance of alternative systems does not permit the development of such a comparison.

Capital Costs

The capital costs of control by PuraSiv Hg adsorption were generated from data available on actual operating systems and from data provided by UCC. Where actual economic data were lacking, conceptual designs based on known process operating characteristics were performed. In these conceptual designs the module technique recommended by Guthrie[24,25] was used. Briefly, this approach to capital cost estimation involves the use of "experience" multipliers to obtain the installed costs of major components of a processing system from known purchased equipment costs. As explained in Appendix B, the installed equipment costs obtained in this manner include the costs of foundations, piping, instrumentation, insulation, and paint. The estimates of capital cost reported would normally be correct to within a ±30 percent range that is characteristic of such estimates.[26] The costs reported are end-of-1974 estimates for a value of the Marshall and Stevens Index of 398. Where conceptual designs were necessary (as in the case of cooling/demisting) the capital costs were estimated for plants of 100 and 750 TPD capacity, this range representing 87 percent of the mercury cell-chlorine plants.

A conceptual design for the cooling/demisting step was performed in order to obtain the incremental capital and operating costs incurred by recycling the regeneration gas in PuraSiv Hg adsorption. The cost estimates obtained from the conceptual design were about 50

percent lower than those supplied by UCC.[13] The actual cost for a PuraSiv Hg adsorption system was found to be 70 percent higher than the estimates reported by UCC for a 750 TPD plant.[17] The estimated capital costs for cooling and demisting and PuraSiv Hg adsorption are given in Table 5. Appendix B outlines how they were obtained. After the addition of the incremental (15 percent) costs of higher cooling and demisting capacity which is necessary in the case of PuraSiv Hg adsorption, it was found that the capital costs were in the range of 853 and 313 dollars per TPD for plants with chlorine capacities ranging from 100 to 750 TPD.

Operating and Maintenance Costs

The operating and maintenance (O&M) costs include those incurred annually for (1) operating labor, (2) cooling water, electricity, and steam, (3) raw materials and chemicals, (4) local property taxes and insurance, and (5) maintenance labor and materials. Details of the estimated O&M costs for cooling/demisting and PuraSiv Hg adsorption and the method by which they were obtained are given in Appendix B.

The PuraSiv Hg adsorption process is a mercury recovery process. Therefore, a credit for mercury recovery was included. Since primary and secondary cooling are necessary precursors to the adsorption processes, a mercury credit was not taken for the former. The O&M costs of PuraSiv Hg adsorption (including costs of additional cooling/demisting capacity) were found to vary between 0.24 and 0.14 dollars per ton of Cl_2 for plants in the chlorine capacity range of 100 to 750 TPD. A summary of O&M costs is given in Table 6.

Total Annual Costs of PuraSiv Hg Adsorption

The total annual costs of control by PuraSiv Hg adsorption consist of the sum of the operating and maintenance costs, adsorbent replacement costs, and costs incurred for depreciation of the capital investment over its life. Furthermore, 15 percent of the depreciation

TABLE 5. CAPITAL COSTS OF COOLING/DEMISTING AND PURASIV HG ADSORPTION

Cl_2 Capacity		Capital Costs, $1000			
TPD	Thousand Tons per Year	Cooling/ Demisting	Incremental Cooling/ Demisting Costs Attributed to PuraSiv Hg[a]	PuraSiv Hg Adsorption	Total PuraSiv Hg and Incremental Cooling/Demisting[b]
100	34.7	143.0	14.3	71.0	85.3
250	86.7	269.6	26.7	107.6	134.3
500	173.4	435.6	43.6	147.4	191.0
600	208.0	494.1	49.4	160.1	209.5
750	260.0	576.6	57.7	177.2	234.9

(a) Obtained by computing the difference in capital costs between a plant of the stated capacity and another that is 15 percent larger. Thus the incremental cost at 100 TPD is $5907(100)^{0.692}[(1.15)^{0.692} - 1]$.

(b) Total includes PuraSiv Hg adsorption and incremental cooling/demisting at stated capacity. Depreciation costs computed from numbers in this column are given in Table 6.

TABLE 6. O&M COSTS OF PURASIV ADSORPTION

Cl_2 Capacity Thousand Tons per year	Depreciation $1000[a]	Total O&M Costs of PuraSiv Hg Adsorption Including Incremental Cooling/Demisting Costs, $1000	PuraSiv Hg Adsorbent Replacement Costs, $1000	Total Annual Cost of PuraSiv Hg Adsorption $1000 per year[b]	Costs of PuraSiv Hg Adsorption Per Ton of Cl_2, $
34.7	8.5	8.2	3.6	20.3	0.58
86.7	13.4	15.2	9.0	37.6	0.43
173.4	19.1	25.8	18.0	62.9	0.36
208.0	20.9	30.2	21.6	72.7	0.35
260.0	23.5	35.7	27.0	86.2	0.33

(a) Depreciation computed using capital costs in Column 6 of Table 5 assuming 10 year period.

(b) Includes depreciation.

cost of cooling/demisting needs to be added for reasons previously mentioned.

The capital investment for all processes was depreciated over a period of 10 years. This is an average equipment life in the chemical process industries.[26] The length of the adsorbent guarantee of 3 years was taken as the life of the adsorbent. Table 6 also gives the variation with capacity of the annual costs and the costs per ton of chlorine produced. In the capacity range of 100 to 750 TPD it is seen that the costs of PuraSiv Hg adsorption per ton of Cl_2 will vary between $0.58 and $0.33.

CONCLUSIONS AND RECOMMENDATIONS

The data generated from EPA-sponsored tests together with other available information seem to indicate that PuraSiv Hg adsorption is effective in the removal of mercury vapor present in concentrations of the order of 1500 ppbv from the hydrogen by-product stream obtained in the manufacture of chlorine by the mercury-cell process. Removal to levels below 60 ppbv was observed in the above-mentioned tests. There is evidence that sulfur-impregnated activated carbon absorption and depleted brine scrubbing may be effective in removal of the pollutant from the hydrogen by-product stream. However, testing of the other systems for performance is believed to be necessary at this time in order to clearly define those technologies and to establish their capabilities to decrease mercury concentrations to desirable levels (below 60 ppbv). Operators and vendors of treated activated carbon control systems claim that such levels of mercury concentration are easily achievable. Likewise the operator of a depleted-brine scrubbing system (in-house design) claims maximum effluent mercury emissions of 0.03 lb per day from the hydrogen generated in a 150 TPD chlorine plant (about 30 ppbv). Apparently this is being achieved with one-step cooling of the stream to 75 to 80 F. It also is claimed that chlorine concentration in the gaseous effluent from the depleted brine scrubber is so low that caustic scrubbing has been deemed unnecessary.

When the operator of a mercury-cell chlorine process is faced with the problem of choosing a mercury control process, the factors which

are most likely to influence his decision as to which control process is most attractive are

(1) Performance

(2) Reliability

(3) Economic feasibility relative to other processes

(4) Ease of operation and flexibility of design.

As to performance, PuraSiv Hg adsorption does seem to achieve average mercury effluent concentrations lower than 60 ppbv after two years of operating such an adsorption system. This has been observed in the testing of a unit designed to control mercury vapor in a 200 TPD chlorine plant. This has been found to be true from data obtained by the monitoring of adsorber effluent mercury concentration in three out of five adsorption cycles. In the two cycles where the guaranteed level of 60 ppbv was not achieved, the departure amounted to 60 percent in the first and 25 percent in the second. This departure may be attributed to either operating the adsorption unit at levels above those recommended by the design value with respect to hydrogen flow rate and to insufficient cooling of the hydrogen stream prior to mercury adsorption at the time of testing. Cooling to 71 F was employed instead of the recommended 60 F. Evidence accumulated from the operators and/or vendors of depleted brine and treated activated carbon adsorption systems indicates that these processes are potentially capable of achieving the same level of control as PuraSiv Hg adsorption.

From available information on the PuraSiv adsorption system, an availability greater than 95 percent may be inferred. The process involves a relatively simple equipment layout and the materials of construction are not highly specialized. Carbon steel is used throughout. The adsorption system is easy to operate and can be designed in such a manner that a high degree of automation may be achieved.

In summary, it is concluded that

(1) PuraSiv Hg adsorption is a technically viable and feasible mercury control alternative of the end-box and hydrogen by-product streams in mercury-cell chlorine plants

(2) Depleted brine scrubbing and treated activated carbon adsorption are potentially feasible mercury control processes in mercury-cell chlorine plants

(3) The economics of PuraSiv Hg adsorption are such that the total annual costs are in the range of 0.58 to 0.33 dollars per ton of Cl_2 for plant capacities in the range of 100 to 750 TPD with respect to chlorine production. These cost estimates are based on an adsorbent life of three years as guaranteed by UCC. The vendors guarantee of adsorbent life could not be independently verified. However, in EPA testing of a PuraSiv Hg system, the adsorbent was found effective after two years of system operation.

On the basis of this study it is recommended that an engineering analysis similar to the study at hand be performed for depleted brine scrubbing and treated activated carbon adsorption.

REFERENCES

(1) Shreve, R. N., "Chemical Process Industries", Third Edition, McGraw-Hill, New York (1967).

(2) Anonymous, "Atmospheric Emissions from Chlor-Alkali Manufacture", A cooperative study project MCA & PHS, Publ. No. AP 344, EPA (January, 1971).

(3) Anonymous, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category", Reported prepared for Office of Air and Water Programs, U.S. EPA, Publ. No. EPA-440/1-74-007-a (March, 1974).

(4) Stambaugh, E. P. and Hall, E. H., "Topical Report on Basis for National Emissions Standards on Mercury", to Office of Air Programs, U.S. EPA, Contract No. EHSD 71-33 (June 15, 1971).

(5) Anonymous, "The Cost of Clean Air, 1974", Final Report to U.S. EPA by Battelle's Columbus Laboratories under Contract No. 69-01-1538 (January 15, 1974).

(6) Anonymous, "Can Chloride Cutbacks Hold the Price Line?", Chemical Week (March 12, 1975).

(7) Laubusch, E., The Chlorine Institute, personal communication (January and February, 1975).

(8) Anonymous, "Control Techniques for Mercury Emissions from Extraction and Chlor-Alkali Plants", U.S. EPA, Office of Air Programs, Research Triangle Park, North Carolina, Publ. No. AP-118 (February, 1973).

(9) Federal Register, 38 (66), 8831 (April 6, 1973).

(10) Anonymous, American Metal Market (October 29, 1974).

(11) Anonymous, "Engineering Analysis of Emissions Control Technology for Sulfuric Acid Manufacturing Processes", Final Report to PHS, US DHEW, Contract CPA22-69-81 (March, 1970).

(12) Chehaske, J. T. and Cline, J. R., "Testing of a Molecular Sieve Used to Control Mercury Emissions from a Chlor-Alkali Plant", Report to EPA, Control Systems Laboratory, Research Triangle Park, North Carolina, Contract No. 68-02-1406, Task No. 3 (January, 1975).

(13) Based on information made available to Battelle's Columbus Laboratories by Union Carbide Corporation in January and February, 1975.

REFERENCES
(Continued)

(14) Istas, L. J., Manager, Engineering, Pennwalt Corporation, Calvert City, Kentucky, letter to M. Y. Anastas (February 5, 1975).

(15) Cunniff, F. T., Manager - Product Development, Calgon Corporation, Pittsburgh, Pennsylvania, letter to M. Y. Anastas (March 26, 1975).

(16) Dreibelbis, J. A. and Joyce, R. S., "Method of Removing Mercury Vapor from Gases", U.S. Patent 3,194,629 (July 13, 1965).

(17) Clapperton, J. A., Manager of Manufacturing Industrial Chemicals, PPG Industries, Pittsburgh, Pennsylvania, letter to M. Y. Anastas (February 28, 1975).

(18) Spomer, M., BASF Wyandotte, Port Edwards, Wisconsin, communication with M. Y. Anastas (April 3, 1974).

(19) Breck, D. W., "Zeolite Molecular Sieves - Structure Chemistry and Use", John Wiley, New York (1974).

(20) Barrer, R. M. and Woodhead, M., transactions of the Faraday Society, 44, p 1001 (1948).

(21) Logan, W. R., "Mercury Removal from Hydrogen Gas Streams, Journal of Applied Chemistry, 16, p 285 (October, 1966).

(22) Collins, J. J., Miller, W. C., and Philcox, J. E., "The PuraSiv Hg Removal and Recovery", paper presented at the 65th Annual Meeting of the Air Pollution Control Association, Miami Beach, Florida (June, 1972).

(23) Martin, D. A. and Brantley, F. E., "Selective Adsorption and Recovery of Sulfur Dioxide from Industrial Gases by Using Synthetic Zeolites", U.S. DOI, Bureau of Mines, RI 6321 (1963).

(24) Guthrie, K. M., "Capital Cost Estimating", Chemical Engineering (March 24, 1969).

(25) Guthrie, K. M., Process Plant Estimating Evaluation and Control, Craftsman Book Company of America, Solana Beach, California (1974).

(26) Peters, M. S. and Timmerhaus, K. D., Plant Design and Economics for Chemical Engineers, 2nd Edition, McGraw-Hill, New York (1968).

APPENDIX A

CALCULATION OF AVERAGE MERCURY CONCENTRATIONS AND AVERAGE DAILY EMISSIONS IN MOLECULAR SIEVE ADSORBER OUTLET

Data on the 2-hour average mercury concentration (in mg per Nm^3) in the adsorber outlet obtained from Reference 12 was plotted versus cycle time on semi-log graph paper. The average concentration as reported was considered to represent the average time in the interval. A smooth curve was drawn through the points and extrapolated to both ends of the cycle, namely, 0 and 24 hours. The extrapolation was such that the cycle end points of the outlet concentration profile did not exceed the inlet concentration. Plots of the outlet concentration profiles for cycles 1 through 5 are given in Figures A-1 to A-5.

The average concentration was obtained by integration of the outlet concentration profile according to the expression

$$H_{ave} = \frac{1}{\theta_2 - \theta_1} \int_{0_1}^{\theta_2} H(\theta)d\theta \qquad (A\text{-}1) \quad .$$

Where H is the 2-hour average concentration and θ is the cycle time in hours. Linear portions of the semi-log plot were fitted to the equation

$$H(\theta) = E\ 10^{1\theta} \qquad (A\text{-}2) \quad .$$

Integration of this function gives

$$I = \int_{\theta_1}^{\theta_2} H(\theta)d\theta = \frac{E}{2.3031} \left(10^{1\theta}2 - 10^{1\theta}1\right) \qquad (A\text{-}3) \quad .$$

Where the curve is not linear it was divided into smaller linear segments to which the equations given above were applied. The cycle average concentration was obtained by summing the I's and dividing by the cycle time of 24-hours. An example calculation is given for cycle 2 in Table A-1. The average concentration obtained was 0.62 mg/Nm^3.

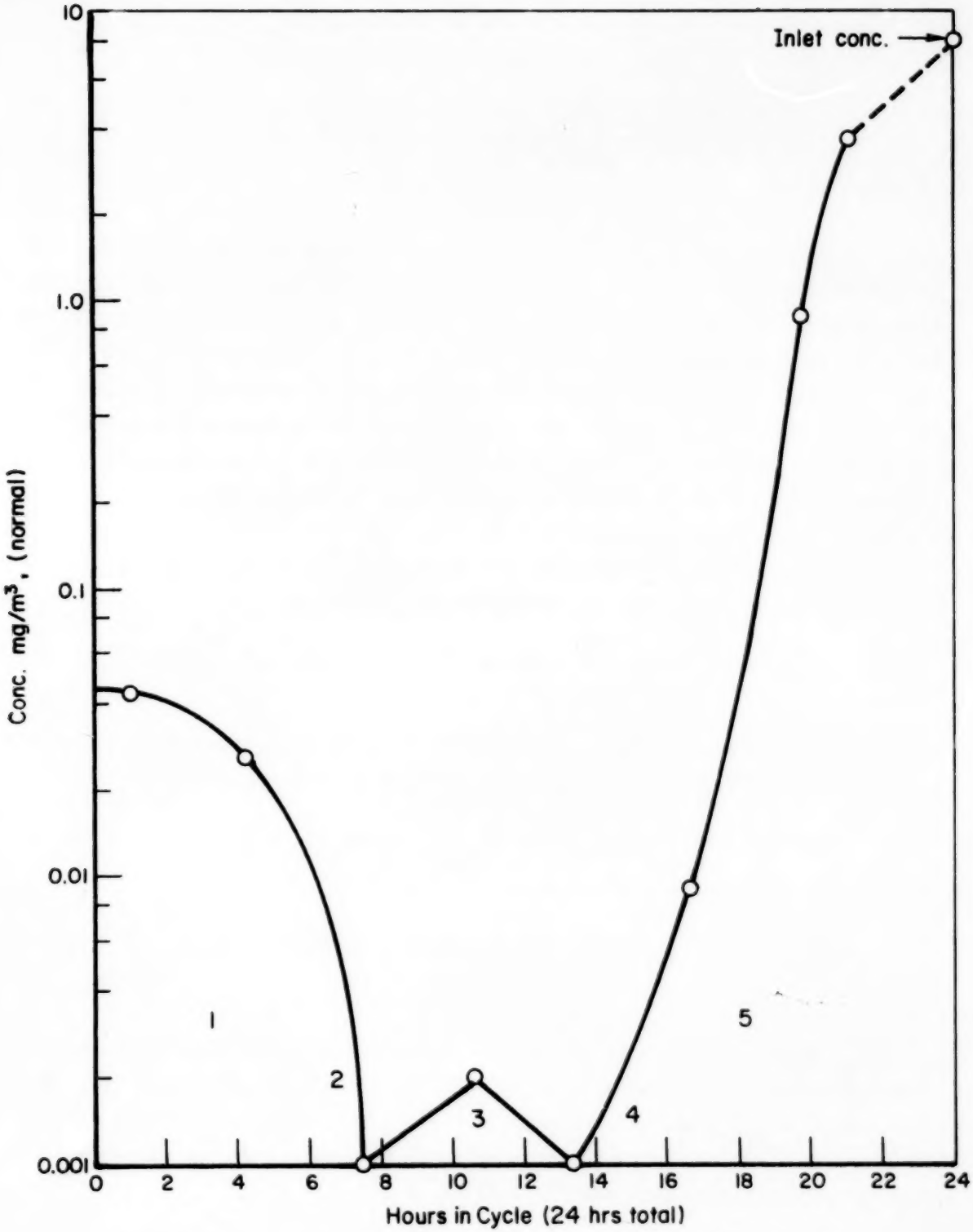


FIGURE A-1. EFFLUENT MERCURY CONC. FROM PURASIV CONTROL UNIT
Date: 24-25, 1975
Cycle: 1
Plant: Sobin - Orrington, Maine

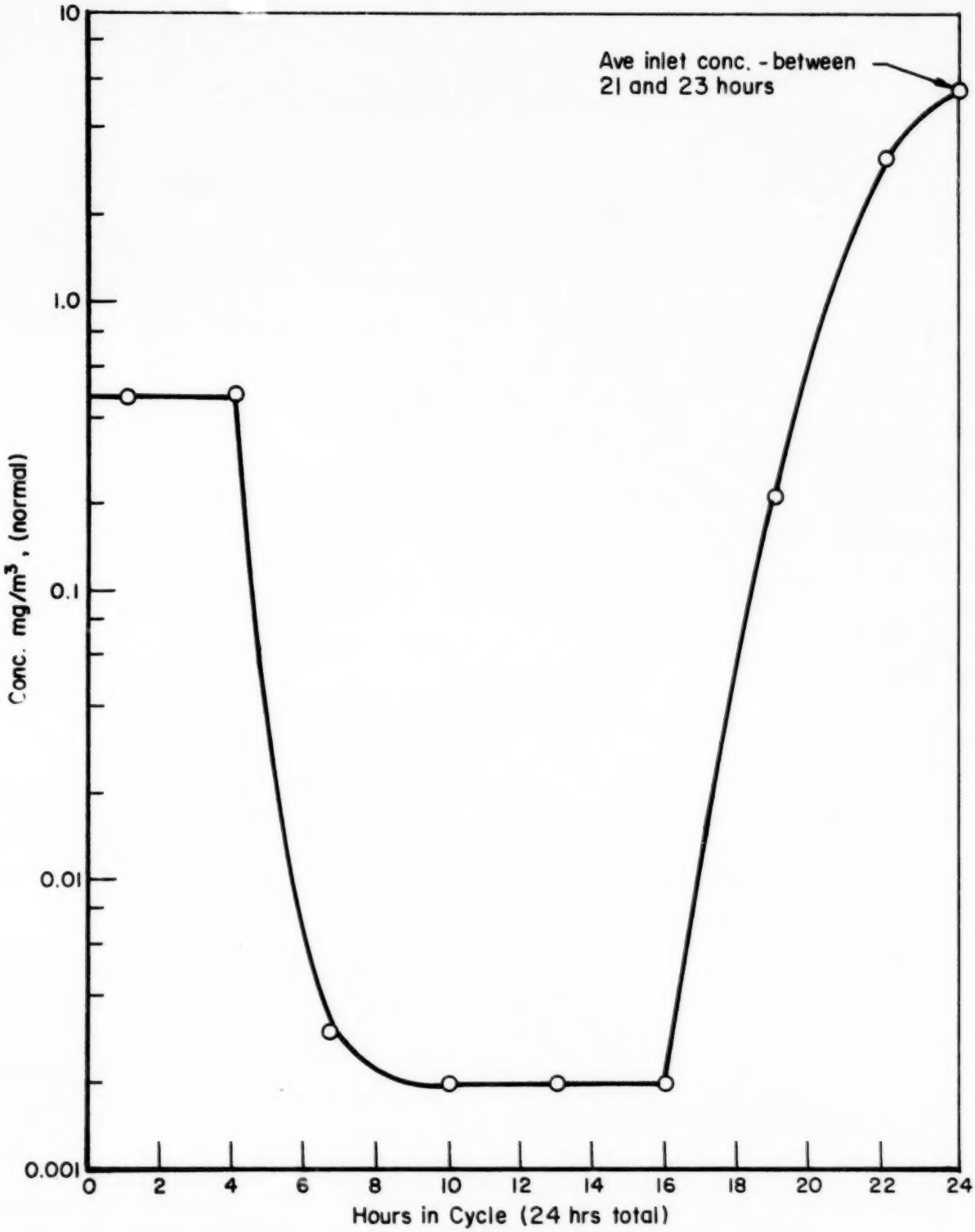


FIGURE A-2. EFFLUENT MERCURY CONC. FROM PURASIV CONTROL UNIT

Date: 25-26, 1975
Cycle: 2 - Adsorber 2
Plant: Sobin - Orrington, Maine

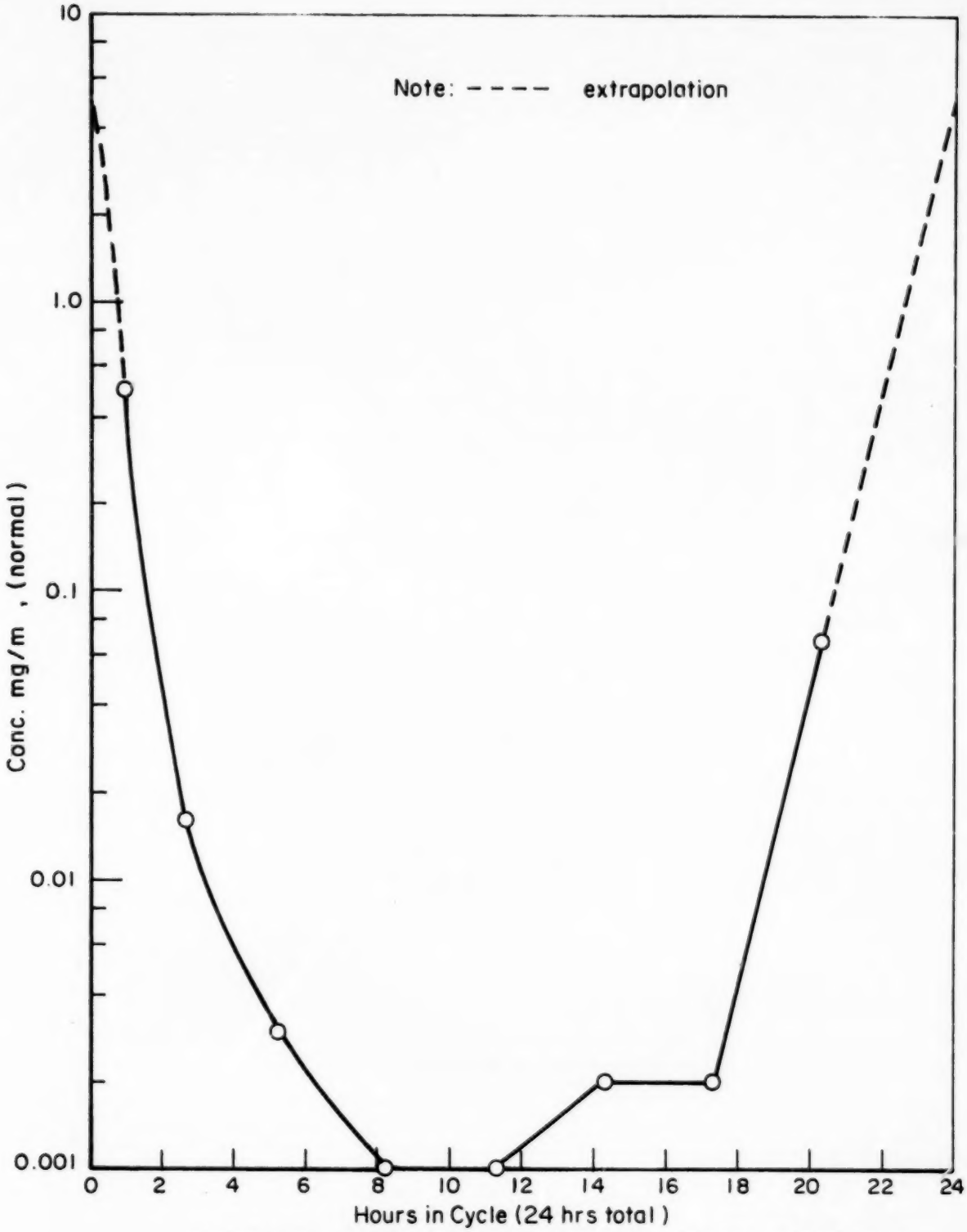


FIGURE A-3. EFFLUENT MERCURY CONC. FROM PURASIV CONTROL UNIT

Date: 26-27, 1975
Cycle: 3
Plant: Sobin - Orrington, Maine

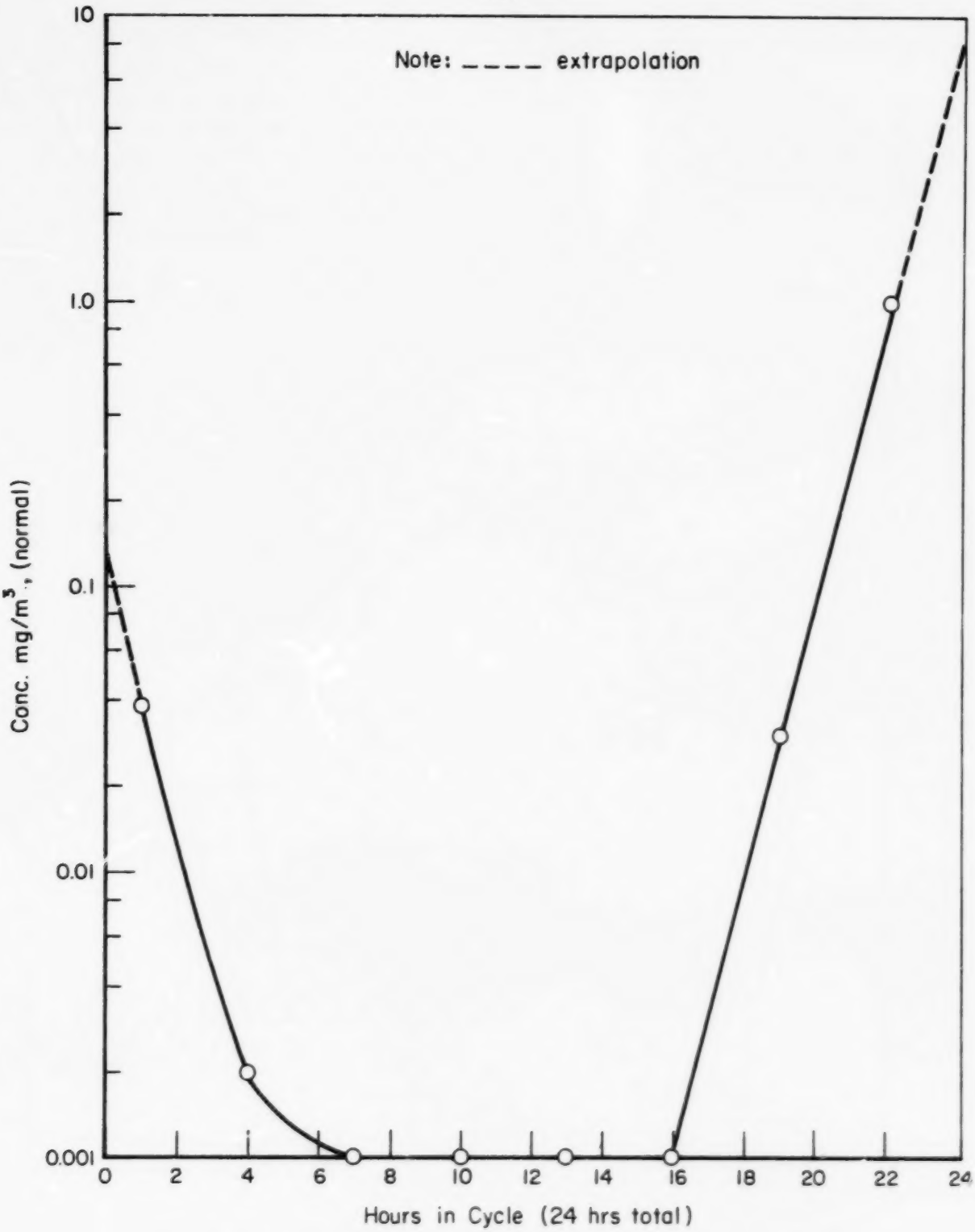


FIGURE A-4. EFFLUENT MERCURY CONC. FROM PURASIV CONTROL UNIT

Date: September 27-28, 1974
Cycle: 4
Plant: Sobin - Orrington, Maine

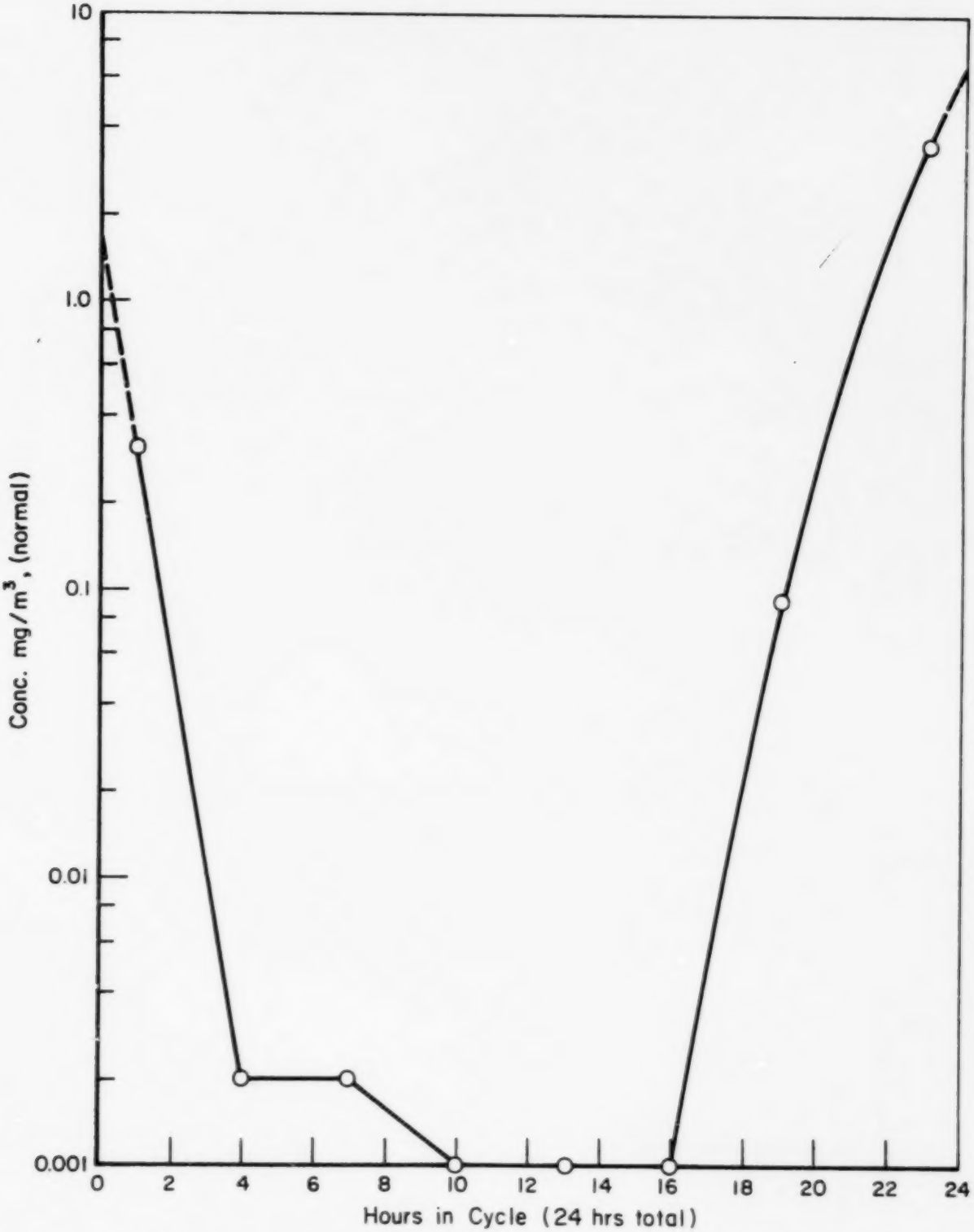


FIGURE A-5. EFFLUENT MERCURY CONC. FROM PURASIV CONTROL UNIT
Date: September 28-29, 1974
Cycle: 5
Plant: Sobin - Orrington, Maine

TABLE A-1. CALCULATION OF AVERAGE MERCURY CONCENTRATION FOR CYCLE

Segment	θ_1	θ_2	H_1	H_2	I
1	0	4	0.48	0.48	1.920
2	4	6	0.48	0.0062	0.218
3	6	8	0.006	0.0022	0.008
4	8	16	0.002	0.002	0.016
5	16	18	0.002	0.06	0.034
6	18	20	0.06	0.65	0.495
7	20	22	0.65	3.4	3.320
8	22	24	3.4	5.5	8.848

$\Sigma I = 14.86$

$H_{ave} = \frac{14.86}{24} = 0.62 \text{ mg/Nm}^3$

The daily mercury emission was obtained by multiplication of the average cycle concentration with the total hydrogen gas flow leaving the process computed from the cycle average chlorine production in tons per hour. Thus for cycle 2:

Nm^3 [70 F and 1 atm] per day

= 7492.0 X (TPD) average

= 7492.0 X 7.64

= 57,240

$$\text{grams Hg per day} = \frac{H_{ave} \times Nm^3 \text{ per day}}{1000}$$

$$= \frac{0.62 \times 57,240}{1000}$$

= 35.4

ppbv - Hg = $120.65 \times H_{ave}$

= 75

For the other cycles the results are given in Table 3.

APPENDIX B

CAPITAL, OPERATING AND MAINTENANCE, AND ANNUAL COSTS OF MERCURY CONTROL PROCESSES

Capital Costs

Where actual economic data were lacking, conceptual designs based on schematic flow sheets were performed for the mercury removal processes considered. The capital costs were obtained from sizing process equipment for a 100 TPD plant and obtaining the installed costs of major equipment using Guthrie's modular technique.[1,2] The equipment cost for a 750 TPD plant was obtained in a similar manner. The capital costs for the 100 and 750 TPD cases were fitted to the equation:

$$C = A_1 (TPD)^n \qquad \text{(B-1)}$$

The conceptual designs were carried out for cooling/demisting (without recycle) and molecular sieve and treated activated carbon adsorption only. The capital costs for depleted brine scrubbing were obtained from published data[3] and data supplied by PPG.[4]

Cooling/Demisting

This step involves the use of five major items of equipment. The first was cooling of the hydrogen by-product stream from the decomposer at 180 F to 110 F at a pressure of 1 atm, using 80 F cooling water, in a shell and tube heat exchanger. The second is a wire-mesh pad mist separator which in sulfuric acid mist removal applications is capable of removing nearly 100 percent of mist particles 3 microns in diameter or larger but removes only 15 to 30 percent of particles less than 3 microns in diameter. The third item of equipment is a water-sealed rotary blower followed by a knock-out drum in which pressure of the gas is increased to about 20.7 psia. The gas is then cooled to 60 F in a shell and tube exchanger using a chilled brine as coolant. A tubular-type mist eliminator

which reportedly removes 99+ percent of particles smaller than 3 microns follows the secondary cooler.

A list of equipment and associated costs appears in Table B-1. All costs were updated to a Marshall and Stevens installed equipment index of 398. Unless indicated otherwise all costs were obtained from Reference 25 in the text. The capital costs obtained for cooling/demisting were found to follow relation:

$$C_{CD} = 5907\ (TPD)^{0.692} \qquad (B\text{-}2)$$

where C_{CD} is the cost in dollars and TPD is the daily chlorine capacity in tons. This capital cost/capacity relation is graphically displayed in Figure B-1.

PuraSiv Hg Adsorption

The PuraSiv Hg adsorption system consists of (1) a steam heated preheater in which the gas to the adsorber is heated to approximately 100 F and (2) two vessels in which at any given time adsorption of mercury is taking place in one and regeneration of the adsorbent is taking place in the other. A portion (15 percent assumed) of the gas leaving the adsorber is heated to a temperature above 500 F in an electrical heater and routed to the vessel undergoing regeneration. The gas effluent from this vessel is cooled to more than 100 F in a shell and tube heat exchanger using 80 F cooling water. A list of equipment and estimated costs by the Guthrie method appears in Table B-2.

The costs supplied by UCC rather than those generated through the conceptual design were used. A linear log-log relation was assumed between the 100 and 750 TPD cases. This led to the expression:

$$C_{MS} = 8775\ (TPD)^{0.454}. \qquad (B\text{-}3)$$

Because of the recycle of regeneration gas through the cooling/demisting module, a 15 percent increase in the capacity of that unit will be required. Therefore, the capital costs of PuraSiv Hg adsorption at any plant capacity are those given by Equation B-3 in

TABLE B-1. CAPITAL COSTS OF COOLING/DEMISTING AND LIST OF EQUIPMENT

	100 TPD		750 TPD	
	Size	Cost, $1,000	Size	Cost, $1,000
Primary Cooler	400 ft^2 [a]	16	3,000 ft	62
Wire Mesh Pad Demister	900 cfm	18 [b]	6,750 cfm	65
Rotary Blower	900 cfm	12 [c]	6,750 cfm	67 [c]
Secondary Cooler	100 ft^2 [a]	4	750 ft^2	16
Refrigerator	25 ton	45	187 ton	192
Tubular Type Demister	530 cfm	26 [b]	4,000 cfm	85
Bare Module Cost		121		487
Total Module Cost (18 percent contingency)		143		575

(a) Reference 5.

(b) References 4 and 8 in the text.

(c) Reference 26 in the text.

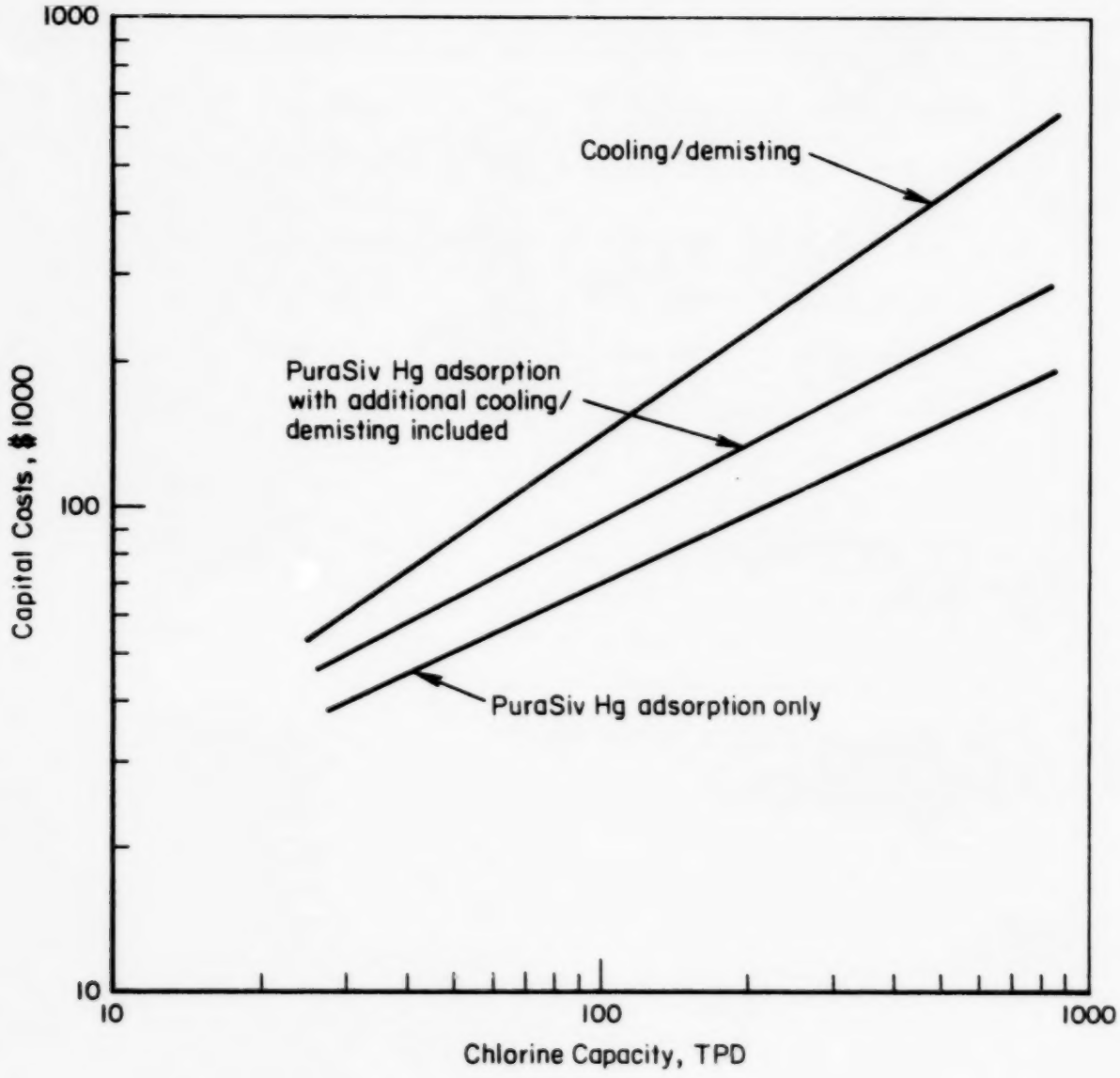


FIGURE B-1. CAPITAL COSTS OF CONTROL OF MERCURY IN THE HYDROGEN BYPRODUCT STREAM

TABLE B-2. CAPITAL COSTS AND LIST OF EQUIPMENT FOR PURASIV HG ADSORPTION

Major Equipment	100 TPD Size	100 TPD Cost, $1000	750 TPD Size	750 TPD Cost, $1000
Preheater	10 ft^2	1	75 ft^2	5
Adsorber vessels (2)	4´ϕ x 11´	35	10´ϕ x 11´	80
Regeneration gas heater	26KW	Nominal	200KW	5
Regeneration gas cooler	28 ft^2	1	213 ft^2	10
Bare module		37		100
Total module 18 percent contingency		44		118
Cost given by UCC		69		175

addition to the capital costs additional for cooling/demisting. The cost/capacity relation is displayed in Figure B-1.

Adsorbent requirements for the process are such that a 3-year replacement is necessary at a cost/capacity variation given by

$$C_{am} = 108 \text{ TPD.} \qquad \text{(B-4)}$$

Operating and Maintenance Costs

Operating and maintenance costs include (1) operating labor; (2) maintenance; (3) utilities including water, electricity, and low pressure steam; and (4) taxes and insurance. An operating rate of 95 percent (or 8,322 hours per year) was assumed. The values of the above items used in computing the O&M costs for the various control processes are summarized in Table B-3.

All processes considered recover mercury. Therefore, a credit for mercury recovery was included. For PuraSiv Hg adsorption the mercury is returned immediately and as such can be treated as an annual credit in this case. For purposes of this study, primary and secondary cooling are necessary precursors to the adsorption process. The costs of cooling/demisting, however, affect the adsorption process as it requires a higher capacity for cooling/demisting because of the recycle of the regeneration gas stream. Therefore, taking a mercury credit for secondary cooling/demisting is not feasible.

Cooling/Demisting

Operating labor costs that may be attributed to the mercury processes for this module were assumed negligible since the operation of this unit may be considered as an integral part of operating the manufacturing process. Maintenance requirements were assumed to be 3 percent of capital per year. Taxes and insurance usually amount to 2.5 percent of capital per year.

The utility requirements of this module are detailed in Table B-4 for a 100 TPD plant.

TABLE B-3. BASIS FOR COMPUTATION OF ANNUAL O&M COSTS

	Cooling/ Demisting	PuraSiv Hg Adsorption
Utilities		
Steam (lb/hr per TPD) @ 50¢ per 1000 lb	--	0.32
Cooling water (gpm per TPD) @ 3¢ per 1000 gal	2	0.075
Electricity (kwhr per hr per TPD) @ 1.2¢ per kwhr	0.93	0.26
Labor, $	--	1,000
Maintenance (percent of capital per year)	3.0	2.0
Taxes and insurance (percent of capital per year)	2.5	2.5
Mercury credit (lbs per year per TPD) @ $2.63 per lb	--	4.4

TABLE B-4. UTILITY REQUIREMENTS FOR COOLING/DEMISTING IN A 100 TPD PLANT

Equipment	Duty	Utility	Rate
Primary boiler	2 MMBtu/hr	80 F, cooling water	200 gpm
Rotary blower	37.5hp[(a)]	Electricity	$\frac{37.5\text{hphr}}{\text{hr}}$
Refrigerator	62.5hp	Electricity	$\frac{62.5\text{hphr}}{\text{hr}}$

(a) Reference 5.

At cooling water costs of 3¢/1000 gal, the annual costs of cooling water are given by:

$$\frac{\$}{\text{year}} = \frac{200 \text{ gpm}}{100 \text{ TPD}} \times \text{TPD} \times \frac{60 \text{ min}}{\text{hr}} \times 8{,}322 \frac{\text{hrs}}{\text{yr}} \times \frac{\$0.03}{1000 \text{ gal}} = 30 \times \text{TPD}$$

The annual costs of electricity at 1.2¢ per kwhr and a mechanical efficiency of 80 percent are:

$$\frac{\$}{\text{year}} = \text{TPD} \times \frac{100 \text{ hp}}{100 \text{ TPD}} \times 0.7457 \frac{\text{kwhr}}{\text{hr hr}} \times 8{,}322 \frac{\text{hr}}{\text{yr}} \times \frac{\$0.012}{\text{kwhr}} \times \frac{100}{80}$$

$$= 93 \times \text{TPD}.$$

Therefore, the total O&M costs for this module are:

$$O\&M = 0.055 \times 5907 \, (\text{TPD})^{0.692} + (30 + 93) \text{ TPD}$$

$$O\&M = 325 \, (\text{TPD})^{0.692} + 123 \text{ TPD}.$$

The above relation is graphically displayed in Figure B-2.

PuraSiv Hg Adsorption

Estimates of the annual operating labor costs were obtained from data provided by UCC[6] and PPG[4]. The annual operating labor costs are $1000. Maintenance was assumed to be 2 percent of capital per year. Taxes and insurance are usually 2.5 percent of capital per year.

The utility requirements for the various items of equipment appear in Table B-5.

Annual cooling water costs as they vary with plant capacity are:

$$\frac{\$}{\text{year}} = \frac{7.5 \text{ gpm}}{100 \text{ TPD}} \times \text{TPD} \times 60 \text{ min/hr} \times 8{,}322 \frac{\text{hr}}{\text{yr}} \times \frac{\$0.03}{1000 \text{ gal}}$$

$$= 1.12 \text{ TPD}$$

Annual costs of electricity are

$$\frac{\$}{\text{year}} = \frac{26 \text{ kw}}{100 \text{ TPD}} \times \text{TPD} \times \frac{14 \text{ hrs}}{24 \text{ hrs}} \times 8{,}322 \frac{\text{hr}}{\text{yr}} \times \frac{\$0.012}{\text{kwhr}} = 15.15 \text{ TPD}$$

Annual costs of LP steam at 50 cents per MMBtu are

$$\frac{32 \text{ lb steam}}{100 \text{ TPD}} \times \text{TPD} \times 8{,}322 \frac{\text{hr}}{\text{yr}} \times \frac{50 \text{ cents}}{1000 \text{ lb steam}} = 1.33 \text{ TPD}$$

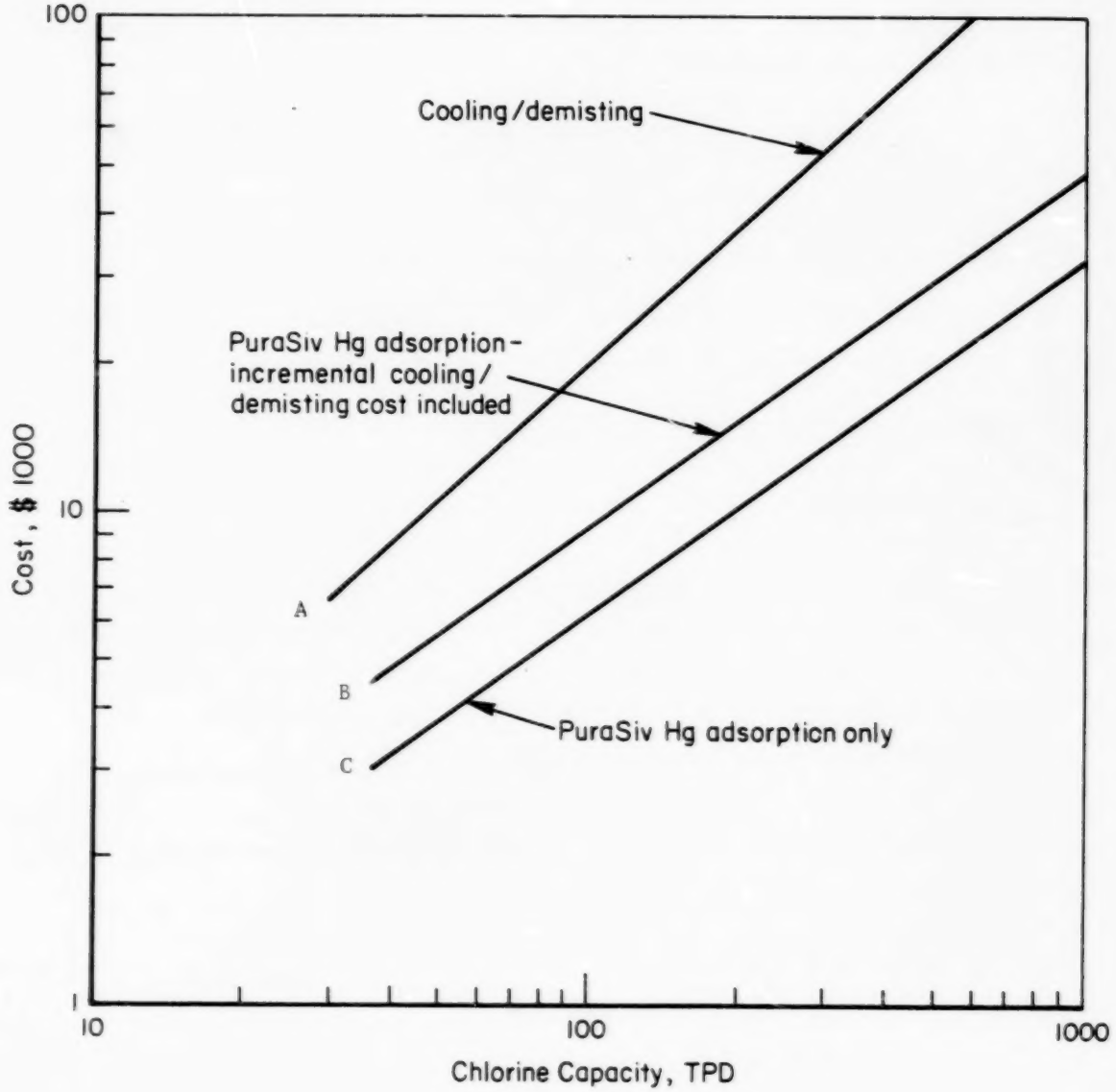


FIGURE B-2. OPERATING AND MAINTENANCE COST FOR MERCURY CONTROL IN HYDROGEN BYPRODUCT STREAM

Table B-5. UTILITY REQUIREMENTS FOR PURASIV HG ADSORPTION IN A 100 TPD PLANT

Equipment	Duty	Utility	Utility Rate
Preheater	32,000 Btu/hr	LP Stream	32 lb/hr
Regeneration Gas Heater	90,000 Btu/hr	Electricity	26 kw
Regeneration Gas Cooler	75,000 Btu/hr	80 F Cooling Water	7.5 gpm

(a) On for only 14 hours out of every 24.

The annual mercury credit amounts to

$$\frac{0.48 \text{ lb per day}}{100 \text{ TPD}} \times 346.75 \frac{\text{day}}{\text{yr}} \times \text{TPD} \times \frac{\$200}{76 \text{ lb}} = 4.4 \text{ TPD}.$$

Therefore, total O&M costs are

$$\text{O\&M} = 483 \text{ (TPD)}^{0.454} + 13.2 \text{ TPD} + 1000. \qquad \text{(B-9)}$$

The above relationship is graphically displayed in Figure B-2. Components of the O&M costs shown in this figure are detailed in Tables B-6, B-7, and B-8 for various Cl_2 capacities.

Total Annual Costs

The total annual costs of PuraSiv Hg adsorption are the sum of the O&M, depreciation, and adsorbent replacement costs.

TABLE B-6. O&M COST COMPONENTS FOR COOLING/DEMISTING $1000 (CURVE A, FIGURE B-2)

Cl_2 Capacity TPD	Labor[a]	Utilities	Maintenance	Taxes and Insurance	Total
100	0	12.3	4.3	3.6	20.2
250	0	30.7	8.1	6.7	45.5
500	0	61.5	13.1	10.9	85.5
600	0	73.8	14.8	12.3	100.9
750	0	92.1	17.3	14.4	123.8

(a) Operating labor for cooling/demisting was assumed to be part of the manufacturing costs.

TABLE B-7. INCREMENTAL O&M COSTS OF COOLING/DEMISTING ATTRIBUTED TO PURASIV HG, $1000

TPD	Labor	Utilities	Maintenance	Taxes and Insurance	Total
100	0	1.8	0.4	0.4	2.6
250	0	4.6	0.8	0.7	6.1
500	0	9.2	1.3	1.1	11.6
600	0	11.1	1.5	1.2	13.8
750	0	13.8	1.7	1.4	16.9

TABLE B-8. O&M COSTS OF PURASIV HG ($1000) EXCLUDING INCREMENTAL COOLING/DEMISTING COSTS (CURVE C, FIGURE B-2)

TPD	Labor	Utilities	Mercury Credit	Maintenance	Taxes and Insurance	Total
100	1.0	1.8	0.4	1.4	1.8	5.6
250	1.0	4.4	1.1	2.1	2.7	9.0
500	1.0	8.8	2.2	2.9	3.7	14.2
600	1.0	10.8	2.6	3.2	4.0	16.4
750	1.0	13.2	3.3	3.5	4.4	18.8

REFERENCES

(1) Guthrie, K. M., "Capital Cost Estimating", Chemical Engineering (March 24, 1969).

(2) Guthrie, K. M., Process Plant Estimating Evaluation and Control, Craftsman Book Company of America, Solana Beach, California (1974).

(3) Anonymous, "Control Techniques for Mercury Emissions from Extraction and Chlor-Alkali Plants", U.S. EPA, Office of Air Programs, Research Triangle Park, North Carolina, Publ. No. AP-118 (February, 1973).

(4) Clapperton, J. A., Manager of Manufacturing Industrial Chemicals, PPG Industries, Pittsburgh, Pennsylvania, letter to M. Y. Anastas (February 28, 1975).

(5) DeAngelis, P., Sobin Chemicals, Orrington, Maine, communication to M. Y. Anastas (March, 1975).

(6) Information made available to Battelle's Columbus Laboratories by Union Carbide Corporation in January and February, 1975.